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.

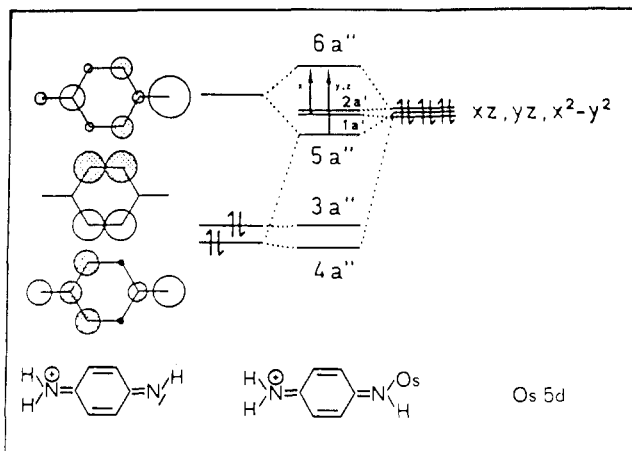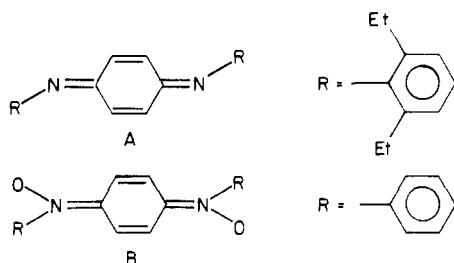**Figure 1.** Hückel MO diagram for $(NH_3)_5M(Hbqd)^{3+}$ using the following parameters: $\alpha(C) = 0$; $\alpha(N) = 0.5\beta$; $\alpha(N^+) = 2\beta$; $\alpha(Ru) = 0.3\beta$; $\alpha(Os) < \alpha(Ru)$; $\beta(Ru-N) = 0.3\beta$; $\beta(C-N) = \beta$; $\beta(C-C) = \beta$ (cf. ref 7).

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:
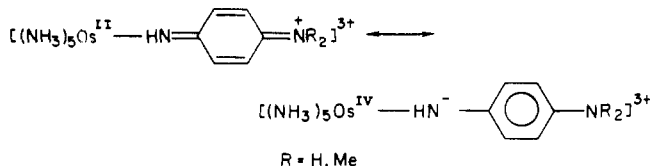
This view is also supported by the chemical shift data of the ammonia protons (Table II). Their signals occur at significantly lower field for the Os than for the Ru complex, indicative of a
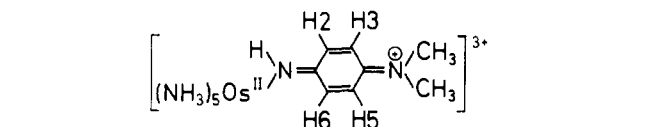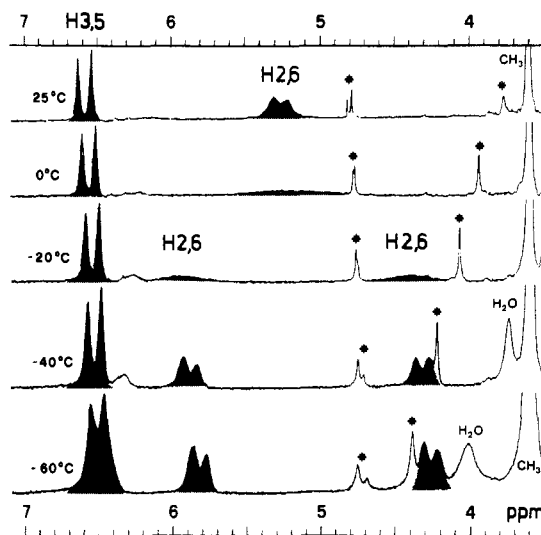
(10) Jackman, L. M., Cotton, F. A., Eds. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1975; pp 203–250.

Figure 2. ^{1}H NMR spectra (Varian XL-100) at different temperatures for $(NH_3)_5Os(N,N$-Me$_2$bqd)$^{3+}$. 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).

higher formal charge on osmium.

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

Steven H. Bertz* and Gary Dabbagh

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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p-toluenesulfinate (**2**), which make these interesting compounds readily available for spectral studies and chemical investigations. Our initial interest in these compounds arose from our investigation of the reactions of organocuprates with aldehyde tosylhydrazones.[6] Sulfinate and nitrogen were eliminated at room temperature (~25 °C) and a new organocopper intermediate was formed that possessed unusually high thermal stability. After 0.5–6 h at 25 °C, treatment with electrophiles gave 70–99% yields of products. One possible explanation that we considered for the thermal stability was the incorporation of sulfinate into the cuprate structure. By preparing organocopper reagents from **1** and **2**, we have found that the sulfinate ligand is not responsible for the observed level of thermal stability;[7] nevertheless, we wish to report the synthesis of these compounds so that other investigators will have access to them for their studies.

A number of synthetic routes starting from copper(I) oxide or a copper(I) halide and the sulfinic acids or their sodium salts in water or tetrahydrofuran were tested. We started with the belief that the best way to obtain dry material suitable for treatment with lithium reagents was to maintain anhydrous conditions throughout; however, we were not able to prepare **2** from the copper(I) halides and sodium p-toluenesulfinate in refluxing tetrahydrofuran. Of the copper(I) halides examined (CuX; X = I, Br, Cl), only the chloride was reactive toward sodium benzenesulfinate in refluxing water; however, the product was contaminated with chloride. The best approach proved to be the addition of 1 equiv wt of sulfuric acid to an aqueous mixture of copper(I) oxide and the sodium sulfinate (eq 1), all of which are commercially available.

$$Cu_2O + 2NaO_2SAr + H_2SO_4 \rightarrow$$
$$2CuO_2SAr + Na_2SO_4 + H_2O \quad (1)$$
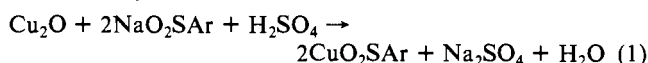
The yellow solid that forms is analytically pure after filtration and vacuum desiccation. These conditions are much milder than those (refluxing alcohol) required to prepare the corresponding copper(I) thiolates from the thiols and copper(I) oxide.[8] They are similar to those (copper(II) carbonate plus the sulfinic acids) that have been used to make the copper(II) sulfinates,[4,5] also isolated as yellow precipitates. One advantage of our procedure is the fact that the sulfinic acid is not isolated or purified. Sulfinic acids have been prepared in high yield by treating alkylcopper reagents with sulfur dioxide followed by hydrolysis.[9] Presumably, copper(I) sulfinates were intermediates; however, they were not isolated or characterized.

The infrared (IR) spectra of the copper(I) sulfinates indicate that their structure is grossly similar to those of the copper(I) carboxylates. The analysis of the IR spectra in the carboxylate series depends upon the difference between the antisymmetric and symmetric C–O stretching vibrations. For a series of copper(I) benzoate complexes, $\Delta\nu$ (cm^{-1}) values of ca. 190, 140, and 130 were assigned to "monodentate", "chelating", and "bridging" coordination, respectively.[2] In sodium benzoate ($\Delta\nu = 143$ cm^{-1}) it was concluded on the basis of polar effects that the CO$_2^-$ group is not symmetrical, but undergoes rapid interconversion between two equivalent, classical structures.[10] We note that this value of $\Delta\nu$ is close to the value for "chelating" coordination. For sodium benzenesulfinate and sodium p-toluenesulfinate, $\Delta\nu$ is ca. 50 cm^{-1} in both the solid state (KBr) and in aqueous solution, which was interpreted in terms of "a resonant sulfinate structure".[11] The respective $\Delta\nu$ values measured for these compounds under our conditions are 47 and 48 cm^{-1}. In **1** and **2**, $\Delta\nu$ is 43 and 41 cm^{-1}, respectively, which is suggestive of "bridged" structures, since this difference is significantly below the value for the sodium salt (cf. corresponding carboxylate values). This conclusion must be re-

garded as tentative, since we do not have a value of $\Delta\nu$ for monodentate coordination and cannot evaluate the significance of $\Delta(\Delta\nu)$ for a more meaningful comparison with the carboxylate series.

X-ray diffraction analysis of a single crystal of tetrakis[copper(I) benzoate] reveals a structure in which each oxygen atom of a carboxylate group bonds to a different Cu atom and each Cu atom is coordinated by two oxygen atoms (from different carboxylate groups) in a 16-membered ring.[12] Whether the structure of **1** is analogous and what perturbations are caused by the substitution of sulfur with its lone pair of electrons for carbon must await the growth of single crystals of **1**, the prospects for which are not good. Compounds **1** and **2** are quite insoluble in most organic solvents, and we have not been able to grow satisfactory crystals from Me$_2$SO, DMF, or nitromethane, in which they appear to be only slightly soluble. Even if it does prove possible to grow crystals from these polar, coordinating solvents, they may well contain solvent of crystallization perturbing the solid-state structure. On the basis of the enhanced stability of **1** and **2** toward decomposition under ambient conditions compared with that of the copper(I) carboxylates,[2] significant structural differences may be anticipated. Indeed, EXAFS spectroscopy indicates that there is a full Cu–S bond in **2** in addition to the Cu–O bonds.[13] In contrast, there is no Cu–S coordination in the analogous copper(II) sulfinate.[13] The presence of both Cu–S bonding and Cu–O coordination in **1** and **2** is not unreasonable in light of the great variety of bonding patterns exhibited by Cu(I).[14]

Experimental Section

IR spectra were obtained on a Perkin-Elmer 597 spectrophotometer. For the sodium salts, it was necessary to fabricate the KBr pellets in a dry nitrogen atmosphere with dry implements and dry materials in order to reproduce the literature values.[11] Compounds **1** and **2** were handled in air without apparent consequence. Melting points were measured by using material sealed in capillaries under nitrogen. Microanalyses were performed by Galbraith Laboratories (Knoxville, TN).

Copper(I) p-Toluenesulfinate. To a solution of 1.78 g (0.01 mol) of p-toluenesulfinic acid, sodium salt (Aldrich, 97%), dissolved in 50 mL of deionized, deoxygenated (nitrogen) water was added 0.71 g (0.005 mol) of Cu$_2$O (Alfa, 99.95%) all at once. Then 0.50 g (0.005 mol) of sulfuric acid (MCB Reagent) diluted to 20 mL with deionized, deoxygenated water was added by syringe pump over 6 h. After the mixture was stirred for 1 day at room temperature under nitrogen, some red solid was still present intermingled with a new yellow solid. After 2 days the fine yellow solid was suspended by gentle swirling and decanted from a small amount of denser red material, which tended to stick to the flask. Suction filtration, drying under nitrogen on the coarse-sintered-glass funnel, and finally drying under vacuum over phosphorus pentoxide yielded 1.9 g (85%) of the product, mp 221–223 °C. Repeating the above experiment with 1.0 g (0.01 mol) of sulfuric acid gave a 70% yield.

Anal. Calcd for C$_7$H$_7$CuO$_2$S: C, 38.44; H, 3.23; Cu, 29.05; S, 14.66. Found: C, 38.41; H, 3.36; Cu, 29.20; S, 14.83. IR (KBr): 3420 (w), 3032 (w), 2915 (w), 1596 (w), 1493 (w), 1394 (w), 1376 (w), 1065 (s), 1005 (s), 964 (s), 809 (s), 704 (m), 652 (m), 640 (m), 632 (m), 587 (m), 496 (m) cm^{-1} (w = weak, m = medium, s = strong).

Copper(I) Benzenesulfinate. Repeating the above procedure with sodium benzenesulfinate gave 67% of a yellow solid, mp 221–222 °C.

Anal. Calcd for C$_6$H$_5$CuO$_2$S: C, 35.20; H, 2.46; Cu, 31.04; S, 15.66. Found: C, 35.47; H, 2.48; Cu, 30.82; S, 15.84. IR (KBr): 3445 (w), 3055 (w), 1444 (m), 1165 (s), 1011 (s), 1004 (s, shoulder), 968 (s), 920 (m), 752 (s), 706 (m), 690 (s), 631 (m), 602 (s), 550 (w), 512 (m), 502 (m) cm^{-1}.

Procedure for Measuring Thermal Stability. Protocols for cleaning glassware[15] and handling reagents[16] have been published. All operations were performed in an inert atmosphere (Ar or N$_2$), and ethereal solvents were freshly distilled from Na/benzophenone. A 25-mL recovery flask was charged with 1.00 mmol of the Cu(I) precursor to be studied, flushed

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with N_2, and sealed with a rubber septum. After 50 μL of decane (internal standard, weighed to 0.1 mg) and 10 mL of ether were added, it was cooled to −50 °C, and 1.00 mmol of BuLi (Aldrich, ~1.5 M solution in hexanes, standardized immediately before use) was added. After 0.5 h at −50 °C, a 1.0-mL sample was withdrawn by using a syringe cooled with dry ice,[16] and it was injected into excess benzoyl chloride in a 2-dram vial that had been purged with N_2 and sealed with a rubber septum. The vial was cooled in dry ice until the sample had been injected, and then it was allowed to warm to room temperature. The reaction mixture was transferred to a −25 °C bath for 0.5 h and the sampling repeated. It was likewise sampled after 0.5 h at 0 °C and 0.5 h at 25 °C. The amount of viable cuprate remaining at each stage was equated with the amount of 1-phenyl-1-pentanone present in the samples taken, as measured by calibrated GLC. For the copper reagent from **1** and BuLi, the yields were 100% (−50 °C), 90% (−25 °C), 85% (0 °C), and 57% (25 °C).

Registry No. 1, 97877-83-3; **2**, 97877-82-2.

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The Tetraamminecopper(II) Complex in Zeolite Y. A Raman Spectroscopic Study

P. K. Dutta* and R. E. Zaykoski

In recent years there has been much interest in the structure and catalytic properties of transition-metal ions and complexes in zeolites.[1] The zeolite matrix can influence the reactivity of metal complexes by the unique steric and electrostatic constraints its cavities can impose. Many spectroscopic studies, including infrared,[2] EPR,[3] EXAFS,[4] and XPS,[5] have been explored to study the bonding of metal complexes within zeolite cavities. Raman spectroscopy, which provides considerable structural information on coordination compounds, has not been exploited for study of metal–zeolite systems, mainly because of the high fluorescence from the matrix.

This preliminary report indicates that, by careful manipulation of metal–zeolite complexes, it is possible to obtain bonding information by spontaneous Raman spectroscopy. We have studied the copper–ammine system because of the extensive EPR[6] and electronic spectroscopic[7] information on these complexes in zeolites. Also, these complexes are active intermediates in the catalytic oxidation of ammonia.[8] It is important to point out that IR spectroscopy of these systems is not very valuable in the low-frequency region, where metal–ligand vibrations are expected.

Experimental Section

Cu–Y zeolite was prepared by ion exchanging zeolite Y (Union Carbide LZY 52) with 0.1 M $Cu(NO_3)_2$ solution. The Cu loading was determined by atomic absorption to be 7.3% by weight.

Pellets of Cu–Y were activated in a greaseless vacuum system by using the procedure described by Lunsford and co-workers.[6] To keep the fluorescence to a minimum, it is important to start the activation at low temperature (100 °C) and gradually increase it stepwise at 100 °C/h to 400 °C. Ammoniation was carried out with anhydrous NH_3 (Matheson)

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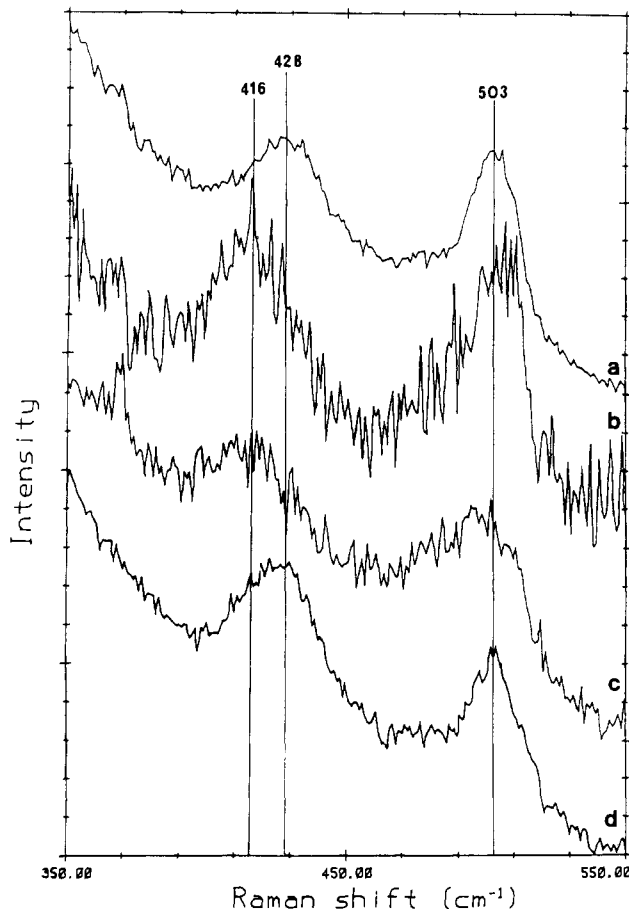
Figure 1. Raman spectra in the Cu–N stretching region: (a) hydrated ion-exchanged $Cu(NH_3)_4^{2+}$–Y; (b) dehydrated CuY + NH_3; (c) dehydrated ion-exchanged $Cu(NH_3)_4^{2+}$–Y; (d) hydrated CuY + NH_3. Laser line = 457.9 nm.

at an ammonia pressure of 400 torr. The pellets were transferred anaerobically to an enclosed Raman spinning cell. The hydration of these samples was carried out over a saturated NH_4Cl solution. The samples were bright blue, with an absorption maximum at ~625 nm.

Ion exchange of Na–Y was carried out with 0.1 M $Cu(NH_3)_4(NO_3)_2$ solution[9] in 1.5 M NH_4OH for 48 h (Cu by weight 5.6%). The washed sample was hydrated over saturated NH_4Cl solution. Dehydration of this sample was carried out by heating at 135 °C for 1 h at 10^{-5} torr, it was ammoniated at 500 torr of NH_3 for 20 min, and the process was repeated four times.

Raman spectra were collected by using a Spex 1403 double monochromator with an RCA C31034 GaAs photomultiplier and photon-counting electronics. The samples were excited with 50–100 mW of the 457.9-nm line of an argon ion laser. Similar spectra were also observed at 514.5 nm. Spectra were scanned in 1-cm⁻¹ steps with collection times of 5 s/wavenumber. All solid samples were spun to avoid any photochemical decomposition and spectra recorded in a 90° configuration. Fluorescence from the zeolite was minimized by working with high-purity chemicals, a greaseless vacuum system, and no contact with plastic ware. The elemental analysis indicates that the concentration of the metal complex in the zeolite that scatters the Raman light corresponds to a solution concentration of 1 mM. The Raman spectra shown in Figure 1 and 2 can be considered as spontaneous Raman spectra (since there are no electronic bands in the vicinity of the laser excitation) and clearly illustrate that, with careful sample handling, it will be possible to obtain Raman spectra of complexes in zeolites at millimolar concentrations. It is important to point out that, for complexes with accessible electronic transitions, resonance-enhanced Raman spectra should provide considerable enhancement in S/N.

Results and Discussion

Lunsford and co-workers, on the basis of EPR and infrared titration studies, have shown that the complex formed by exposing

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