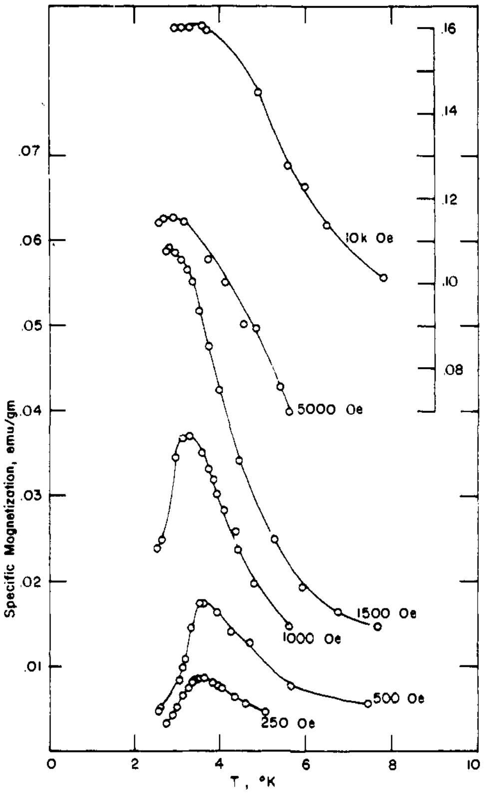

Figure 3: Specific magnetization vs. temperature for several values of applied magnetic field for a powdered sample of $Co[(C_6H_5)CONHCH_2COO]_2{\cdot}5H_2O$. (Right hand ordinate is for the curves at 10 kOe and 5000 Oe. Left hand ordinate is for the curves at 250, 500, 1000, and 1500 Oe.)

the bridge. The chains show no close contact distances to each other with the closest cobalt-cobalt contact distance across two chains, of 6.90 Å along the y cell axis.

The hippurate molecules are bonded to the cobalt through the carboxyl oxygen atoms as has been previously observed in the case of the copper hippurate.[10,11] Figure 2 shows how these molecules fan out from the backbone like alternating rungs of a ladder. The two remaining water molecules in the structure lie between the hippurate steps and have no close contact with the cobalt ions.

Zero field magnetic susceptibility data for the powdered complex were obtained from 2.5 to 80 K. The plot of $1/\chi_M$ vs. T (not shown) was indicative of Curie-Weiss law behavior above 40 K (with $\theta = 32°$ and $C = 0.46$). Between 40 and 10 K a broad minimum, typical of an antiferromagnet, was observed, followed by a sharp, essentially linear decrease in $1/\chi_M$ as the temperature was lowered below 10 K. Susceptibility behavior of this type is expected for a metamagnet. However, the metamagnetic character of the compound is more convincingly exhibited by the temperature dependent magnetization data taken with magnetic fields in the range of 0–10 kOe. Field dependent isothermal magnetization curves (not shown) were obtained from 2.59 to 5.62 K in fields up to 10 kOe. Below 3.14 K S-shaped curves characteristic of metamagnets were observed. Curves of specific magnetization vs. T at constant applied fields are shown in Figure 3. Note that the specific magnetization maximum shifts to lower temperatures as the external field strength is increased, again indicating that the complex exhibits metamagnet behavior rather than a "spin-flop" transition. At an applied field of approximately 1500 Oe, the antiferromagnetic transition disappears and ferromagnetic saturation is observed. These magnetic data are analogous to those reported for the $Co(pyr)_2Cl_2$ system[4-6] which has been interpreted in terms of strong ferromagnetic exchange interactions along the chains and weak antiferromagnetic exchange between chains. Work is presently underway to model the magnetic data via equations developed for Ising linear chains[4] and to relate the exchange phenomena to the observed low temperature optical spectra.

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Reductive Coupling of Adjacent Ligands in a Seven-Coordinate Molybdenum(II) Isocyanide Complex[1]

Sir:

Recently we have synthesized and structurally characterized the seven-coordinate molybdenum(II) complexes $[MoL_7]^{2+}$ and $[MoL_6X]^+$, where L is *tert*-butyl isocyanide and X = Cl, Br, I.[2-5] The structures consist of a capped trigonal prism with either halide or isocyanide as the capping ligand (Figure 1). The short nonbonded contacts between coordinated carbon atoms suggested that ligand migration or coupling reactions, known to occur for other metal isocyanide complexes,[6-9] might be especially facile for these heptacoordinate molybdenum(II) cations.

A suspension containing 3 mmol of red-orange $[(RNC)_6MoI]I$,[3] R = *tert*-butyl, and 10 mmol of zinc dust in tetrahydrofuran was allowed to reflux under nitrogen for 2 h. The final, deep red solution was filtered and the solvent removed in vacuo. Red, air-stable crystals were obtained in 90% yield upon recrystallization from acetone or benezene and diethyl ether. Analytical data were consistent with the empirical formula $(RNC)_6MoI_2H_2$.[10] The infrared spectrum of the compound mulled in carbon tetrachloride had absorptions at 2128 cm^{-1} (br, mult), assigned to terminal isocyanide stretching modes, bands at 1593 and ~1400 cm^{-1} in the C=C and C=N stretching region, two N—H stretching frequencies at 3102 and 3160 cm^{-1}, and an N—H deformation band at 1513 cm^{-1}. The assignment of the N—H stretching bands was verified by a deuterium exchange experiment. They shifted to 2309 and 2359 cm^{-1}, respectively, when the complex was deuterated by shaking a solution of it in chloroform with D_2O for 1 h, separating the layers, and precipitating the product

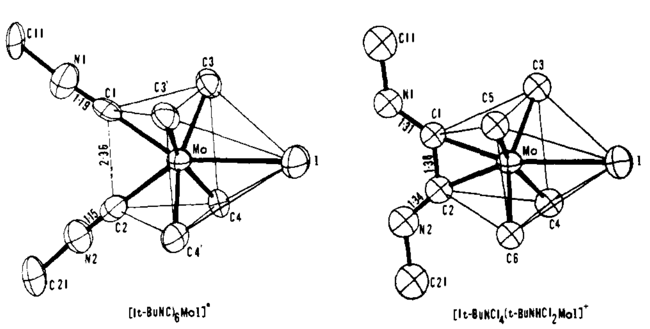
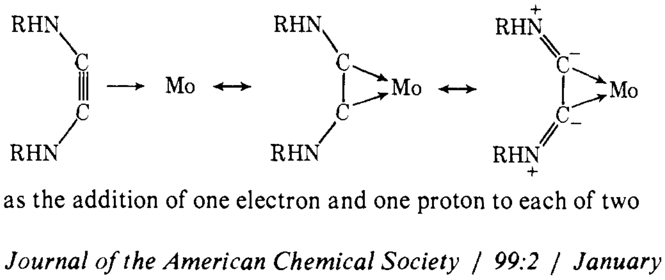


Figure 1. Molecular geometry of the cations in (left) [(*t*-C_4H_9-NC)$_6$MoI]I,[4] the starting material, and (right) [(*t*-$C_4H_9NC)_4$ (*t*-$C_4H_9HN\overset{\cdots}{-}C\overset{\cdots}{-}C\overset{\cdots}{-}NHC_4H_9$-*t*)MoI]I, the product, as determined by x-ray diffraction. Interatomic distances (in Å) shown have estimated standard deviations of 0.03 Å or less.

with ether. The N—H deformation similarly shifted to a lower frequency upon deuteration. The 100-MHz proton NMR spectrum of the compound in $CDCl_3$ showed methyl resonances of the *tert*-butyl groups at δ 1.48 and 1.66 ppm of relative intensities 2:1. A small peak at 9.68 ppm with an integrated intensity about one-thirtieth that of the combined *tert*-butyl resonances provided further confirmation of the empirical formula. This resonance did not appear when the complex was dissolved in acetone-d_6 containing a few drops of D_2O. Pulsed Fourier-transform ^{13}C NMR spectra also revealed two *tert*-butyl environments, with methyl carbon resonances at 29.96 and 30.28 ppm and tertiary carbon shifts of 56.89 and 54.75 ppm, relative intensities 2:1, respectively. The resonances of the carbon atoms of the *tert*-butyl isocyanide ligands bonded to molybdenum appeared at 157.1 ppm, and the chemical shift of the corresponding carbon atoms of the $(LH)_2$ ligand was 192.9 ppm.

An x-ray crystallographic study was required to establish the true nature of the product. Using 4038 observed reflections collected with Mo Kα radiation ($2\theta \leq 55°$), the structure was solved by heavy atom methods and refined to a current value of 0.059 for R_1, the conventional agreement factor.[11] As shown in Figure 1, the molecular geometry is very similar to that of the starting $[(RNC)_6MoI]^+$ cation with one major difference. In the product there is a bond between the two carbon atoms on the edge opposite the capped face. The resulting C-C (1.38 ± 0.02 Å) and C-N (1.33 ± 0.02 Å) distances in the coupled ligand require multiple bond character, and the mean C-N-C angle of 128° is consistent with the presence of N-H bonds. There has not yet been any attempt to locate hydrogen atoms in the difference Fourier maps.

The structural and spectroscopic results indicate that the product of the reductive coupling reaction may be considered as a bis(alkylamino)acetylene derivative with substantial bond delocalization, $RHN\overset{\cdots}{-}C\overset{\cdots}{-}C\overset{\cdots}{-}NHR$.[12] Although the free ligand does not appear to be a known compound,[14] its stability is enhanced by coordination to the molybdenum atom. Regarding the ligand as an acetylene molecule would result in a 16-electron molybdenum(II) cation for which there is some precedence.[15] Alternatively, the complex achieves a closed shell configuration if the ligand is viewed as a dicarbene. These two extremes and one of several possible charged resonance forms are depicted below. We may view the present reaction formally as the addition of one electron and one proton to each of two isocyanide ligands which then couple to one another on the unique edge. Such a process would be similar to carbene formation by addition of H—X across the C≡N triple bond of a coordinated isocyanide ligand.[16] Here the group X is an adjacent carbon atom in the coordination sphere.



Although we emphasize that the mechanism in which two isocyanide ligands are reductively coupled is presently unknown, the reaction may be an example of a higher coordination effect. The close nonbonded contact between the ligands in $[(RNC)_6MoI]^+$ might enhance the propensity for carbon–carbon bond formation. Molecular orbital calculations[17] of d^4 capped trigonal prismatic compounds such as $[(RNC)_6MoI]^+$ show a small positive overlap population between the two ligands on the unique edge of the coordination polyhedron. Further work is in progress to test this and other mechanistic possibilities.

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The Structure of Juncusol. A Novel Cytotoxic Dihydrophenanthrene from the Estuarine Marsh Plant *Juncus roemerianus*[1]

Sir:

The Mississippi salt marsh is an irregularly flooded estuary dominated by the needlerush *Juncus roemerianus* (Juncaceae). Studies by de la Cruz[2] on the ecology of Mississippi salt marsh on the primary production and decomposition of marsh plants have served to focus attention on their value to estuarine animals including those of commercial importance. We therefore have initiated a continuing chemoecological study