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Binuclear Molybdenum Carbonyl Complexes with Bridging 1-Substituted Tetrazole Ligands¹

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Considerable evidence suggests that the tetrazole ring (see Figure 1 for structure and numbering convention) has six π electrons. For example, the crystal structure of 1-methyltetrazole² indicates that N₁ must be essentially sp² hybridized with the lone pair occupying a p orbital perpendicular to the tetrazole ring. Thus, it is conceivable that tetrazoles could form an η^5 complex with an appropriate metal such as observed in (η^5 -C₄H₄NH)Cr(CO)₃.³

An ab initio molecular orbital calculation for tetrazole indicates that the HOMO is a π orbital. However, the photoelectron spectrum for tetrazole does not unequivocally show this to be the case.⁴ Two delocalized σ orbitals and this π orbital have about the same ionization energy.

In an attempt to synthesize a complex involving the tetrazole ring π electrons, the reactions of *fac*-tris(acetonitrile)tricarboxymolybdenum and various 1-substituted tetrazoles were investigated. This investigation did not lead to the observation of an η^5 complex but instead the formation of binuclear molybdenum complexes with η^2 -tetrazole bridging ligands.

Experimental Section

All metal compound syntheses and manipulations were performed with use of standard vacuum line and inert-atmosphere techniques.⁵ All solvents were reagent grade and were purified just prior to use. Acetonitrile was refluxed under purified nitrogen and transferred into the reaction vessel. Diethyl ether was distilled from sodium-benzophenone under a nitrogen atmosphere.

Molybdenum hexacarbonyl was purchased from Pfaltz & Bauer and was used without additional purification. The various 1-substituted tetrazoles were prepared as described previously for 1-phenyltetrazole⁶ (1-PT) and 1-methyltetrazole (1-MT) and 1-cyclohexyltetrazole⁷ (1-CT). The tetrazoles were purified by sublimation. The purity was confirmed by comparing the melting points and infrared spectra with previously reported values.

All infrared spectra were recorded on a Beckman IR-20AX as Nujol and halocarbon mulls between KBr plates and as CH₂Cl₂ solutions in a variable-path-length cell with NaCl windows. The spectra were calibrated with a thin film of polystyrene.

All proton NMR spectra were recorded at room temperature on a Varian EM360 spectrometer at 60 MHz. For the various 1-MT and 1-PT compounds the spectra were run in (CD₃)₂CO solutions, and for the 1-CT compounds the spectra were run in CH₂Cl₂ solutions with tetramethylsilane as an internal standard.

Melting points were recorded in capillaries with a Thiele-Dennis melting point apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of (CO)₃Mo(1-CT)₃Mo(CO)₃. In a typical preparation 198 mg (0.75 mmol) of Mo(CO)₆ was added to 20 mL of acetonitrile in a 50-mL flask. The mixture was allowed to reflux for 3 h or until no more CO was produced. The yellow solution was evaporated to dryness under vacuum, leaving *fac*-Mo(CO)₃(CH₃CN)₃.⁸ To this yellow solid was added 20 mL of CH₂Cl₂. While the mixture was stirred at room temperature, 228 mg (1.50 mmol) of 1-CT was added.

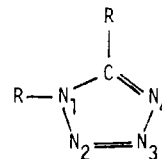


Figure 1. Structure and numbering conventions for tetrazole.

The solution immediately turned orange, and after approximately 15 min a pale yellow precipitate formed. After the reaction was allowed to proceed for an additional 1 h, the solution was filtered, washed three to four times with a total of 50 mL of (C₂H₅)₂O, filtered, and dried under reduced pressure. A total of 306 mg of product, (CO)₃Mo(1-CT)₃Mo(CO)₃, was recovered. This corresponds to an 81% yield based upon the initial amount of Mo(CO)₆. Essentially the same result is observed when the CH₂Cl₂ solution is allowed to reflux for a period of 1-2 h.

Anal. Calcd for C₂₇H₃₆N₁₂O₆Mo₂: C, 39.71; H, 4.45; N, 20.59. Found: C, 39.56; H, 4.64; N, 20.41. The complex decomposes without melting at 145-146 °C. CO vibrational stretches were observed at 1927 and 1813 (s) cm⁻¹ in CH₂Cl₂ and 1921 and 1786 (s, br) cm⁻¹ in Nujol. The tetrazole ring C-H stretch was observed at 3125 cm⁻¹ for 1-CT and at 3165 cm⁻¹ for the 1-CT complex. The ¹H NMR was δ 8.71 (s, ring C-H) for 1-CT and δ 9.28 for the 1-CT complex.

Synthesis of (CO)₃Mo(1-PT)₃. The method used here is the same as that described previously. Typical quantities used were 408 mg (1.55 mmol) of Mo(CO)₆ and 451 mg (3.09 mmol) of 1-phenyltetrazole (1-PT). After the addition of 1-PT to the CH₂Cl₂ solution containing *fac*-Mo(CO)₃(CH₃CN)₃, the solution immediately turned red, and after 10 min an orange precipitate formed. A yield of 534 mg was obtained (86% yield based upon the initial amount of Mo(CO)₆).

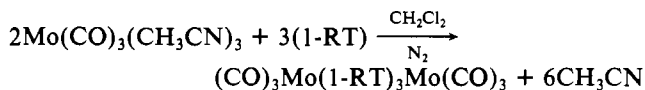
Anal. Calcd for C₂₇H₁₈N₁₂O₆Mo₂: C, 40.61; H, 2.28; N, 21.06. Found: C, 40.01; H, 2.40; N, 20.69. The complex decomposes without melting at 116-118 °C. CO vibrational stretches were observed at 1948 (w), 1922 (s), 1820 (sh), 1804 (s), and 1796 (sh) cm⁻¹ in CH₂Cl₂ and 1932 (sh), 1911 (s), 1825 (sh), 1815 (sh), 1795 (s), and 1770 (sh) cm⁻¹ in Nujol. The ring C-H stretch was observed at 3100 cm⁻¹ for 1-PT and 3124 (br) cm⁻¹ for the complex. The ¹H NMR was δ 9.84 (s, ring C-H) and δ 7.88 (m, phenyl) for 1-PT and δ 10.55 and 8.00 for the complex.

Synthesis of (CO)₃Mo(1-MT)₃Mo(CO)₃. Essentially the same method was that used as described above. Typical quantities used were 400 mg (1.52 mmol) of Mo(CO)₆ and 258 mg (3.07 mmol) of 1-methyltetrazole (1-MT). After addition of 1-MT to the CH₂Cl₂ solution a bright yellow precipitate formed. The product was dried by exposure to a vacuum for 2 days at 50 °C. A yield of 483 mg of product was obtained (76% yield based upon the initial amount of Mo(CO)₆).

Anal. Calcd for C₁₂H₁₂N₁₂O₆Mo₂: C, 23.54; H, 1.98. Found: C, 24.50; H, 2.46. The complex decomposes without melting at 125-127 °C. CO vibrational stretches were observed at 1922 (s) and 1805 (s) cm⁻¹ in CH₂Cl₂ and 1912 (s), 1795 (sh), and 1770 (s, br) cm⁻¹ in Nujol. The ring C-H stretch was observed at 3110 cm⁻¹ for 1-MT and 3147 cm⁻¹ for the 1-MT complex. The ¹H NMR was δ 9.16 (s, ring C-H) and δ 4.20 (s, CH₃) for 1-MT and δ 9.88 and 4.43 for the complex.

Discussion

The reaction of *fac*-Mo(CO)₃(CH₃CN)₃ with various 1-substituted tetrazoles in dry CH₂Cl₂ at room temperature yields (CO)₃Mo(1-RT)₃Mo(CO)₃ complexes according to the reaction



for R = CH₃, C₆H₅, and C₆H₁₁.

All of these complexes exhibit little solubility in most common solvents with the exceptions being that the 1-MT and 1-PT complexes are slightly soluble in acetone and dichloromethane and the 1-CT complex is slightly soluble in dichloromethane. In an attempt to find a solvent suitable for proton NMR studies, it was observed that Me₂SO reacts with

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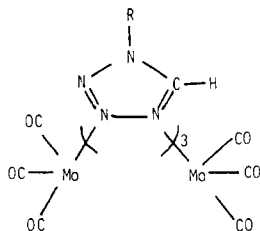


Figure 2. Proposed structure of tris[μ -(1-substituted tetrazole)]bis(tricarbonylmolybdenum).

the 1-PT complex, forming a pale yellow solution. The proton NMR of this solution is characteristic of uncomplexed 1-PT. The infrared spectrum of this solution shows peaks in the carbonyl region that are not assignable to Me_2SO at 1933 (w), 1901 (s), 1825 (m), 1783 (w), and 1753 cm^{-1} (br, s). These absorptions occur at lower energy than those observed for the 1-PT complex. In addition the chemistry is more complex than a simple substitution of 1-PT by Me_2SO to form only *fac*- $\text{Mo}(\text{CO})_3(\text{Me}_2\text{SO})_3$ since the infrared spectrum of this should exhibit only two absorptions assignable to CO. The character of this Me_2SO complex is not known at this time since all attempts to isolate a solid have proven unsuccessful.

All of these complexes as solids show some degree of air stability ranging from 2 h to several days for the 1-MT, 1-PT and 1-CT complexes, respectively. The increased stability can only be attributed to increased size of the tetrazole ring substituents. Solutions of these complexes decompose when exposed to oxygen.

The solution infrared spectral results for the carbonyl region for the 1-CT and 1-MT complexes are indicative of a local C_{3v} symmetry for each molybdenum atom which, along with the observed stoichiometry of the complexes, suggests that each tetrazole is acting as a bridging bidentate ligand. A proposed structure that agrees with the rule of 18 and the stoichiometry is shown in Figure 2. If a C_{3v} symmetry is correct, the higher frequency carbonyl absorption is assigned as the A_1 mode, whereas the lower frequency is assigned as the E mode. The solution IR spectral results for the 1-PT complex and the solid-state forms for all complexes show more than two peaks. This can be interpreted if one assumes that the 1-PT complex and the solid-state complexes exist in more than one isomeric form with symmetries lower than C_{3v} . However the NMR spectrum for the 1-PT complex shows only one peak that can be assigned to the tetrazole ring C-H. Thus at least on the NMR time scale it is apparent that a C_3 axis is present.

Except for the tetrazole ring C-H stretch the remaining portions of the infrared spectra for these tetrazole complexes are quite similar to those observed for the uncomplexed ligands and shift only slightly upon complexation. The increase in the stretching energy upon complexation suggests that the hybrid orbital of carbon used in the formation of the C-H bond acquires more s character. This interpretation is consistent with the NMR observations, which indicate a slight deshielding of the ring C-H resonance upon complexation.

In the case of the 1-PT complex it is possible for the phenyl ring to form a η^6 complex with Mo. The NMR results indicate that this is certainly not the case since the phenyl multiplet is deshielded slightly upon complexation. In complexes such as $\eta^6\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$ the phenyl protons are shielded considerably as compared to those of the free ligand.⁹

The structure shown in Figure 2 suggests that N_3 and N_4 coordinate to the two molybdenum atoms. It is expected that the most basic tetrazole nitrogen would coordinate. The most basic nitrogen has been shown from ^1H and ^{13}C NMR studies of the protonation of 1-phenyltetrazole to be N_4 .¹⁰ This

conclusion is supported in the crystal structure of dichlorobis(1-methyltetrazole)zinc(II),² where N_4 coordinates to zinc. In addition, since little difference is observed between those tetrazole complexes with a substituent with little steric factors ($\text{R} = \text{CH}_3$) and those with large steric factors ($\text{R} = \text{C}_6\text{H}_{11}$), the substituent most likely occupies that space that is in minimum contact with the carbonyl ligands. Such a situation would exist only if N_3 and N_4 coordinate as exhibited in Figure 2.

In summary the reaction between *fac*-tris(acetonitrile)molybdenum tricarbonyl and various 1-substituted tetrazoles resulted in the products $(\text{CO})_3\text{Mo}(1\text{-RT})_3\text{Mo}(\text{CO})_3$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_6\text{H}_{11}$). Elemental analyses and infrared and ^1H NMR spectral data indicate that the tetrazole ligand acts as an η^2 bridging ligand.

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Registry No. $(\text{CO})_3\text{Mo}(1\text{-CT})_3\text{Mo}(\text{CO})_3$, 82150-32-1; $(\text{CO})_3\text{Mo}(1\text{-PT})_3\text{Mo}(\text{CO})_3$, 82150-31-0; $(\text{CO})_3\text{Mo}(1\text{-MT})_3\text{Mo}(\text{CO})_3$, 82150-30-9; $\text{Mo}(\text{CO})_6$, 13939-06-5.

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Electron Transfer. 56. Charge Effects in Inner-Sphere Reductions by Uranium(III)¹

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A recent report³ deals with pairs of (carboxylato)cobalt(III) complexes having similarly branched structures but differing in net charge. It was noted that inner-sphere chromium(II) reductions are more seriously retarded by incorporation of an additional positive center into the carboxyl group than are the corresponding reductions by vanadium(II) and europium(II). This difference was attributed to the mismatch of orbital symmetry between the acceptor π orbitals of the carboxyl bridge in the precursor complex and the migrating e_g electron of Cr^{2+} . A presumed consequence of such a mismatch is that electron transfer requires unsymmetric distortion of the ligand sheath about Cr^{II} , a distortion which is due in large part to water molecules in the second coordination sphere and which becomes less effective when alignment within this sphere is disrupted. An earlier communication⁴ suggested that the migrating electron in 9-coordinate uranium(III) occupies an orbital having symmetry properties akin to those of the e_g orbital in $\text{Cr}(\text{H}_2\text{O})_6^{2+}$, in keeping with the observation⁴ that

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