bond angle deformation or a ring deformation mode. Such a mode would produce a significant dipole moment change along the molecular axis and probably corresponds to the ν_3(A) vibration observed at 771 cm^{-1} in the bidentate carbonato complexes of cobalt(III).[27]

In any event, the observed transition is not satisfactorily explained in terms of a simple O–O stretching mode.

Registry No. $Co(HL)_2O_2ClO_4$, 65956-93-6; $Co(HL)_3(ClO_4)_2$, 15412-27-8.

Supplementary Material Available: A figure showing the IR spectrum of $Co(HL)_2O_2ClO_4$ as a Nujol mull (1 page). Ordering information is given on any current masthead page.

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Preparation of Tetrakis(picolinato)molybdenum(IV)

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The oxidative decarbonylation of tungsten hexacarbonyl by picolinic acid, 2-pyridinecarboxylic acid, to yield tetrakis(picolinato)tungsten(IV), $W(pic)_4$, has recently been reported by us[1] and also by Dorsett and Walton.[2] We have successfully extended this reaction to produce the eight-coordinate complex tetrakis(picolinato)molybdenum(IV). A previous study[2] reports the oxidation of molybdenum hexacarbonyl by picolinic acid to yield exclusively $Mo(pic)_3$ under milder reaction conditions. The successful synthesis of $Mo(pic)_4$ is apparently dependent on the reaction conditions employed, whereas the synthesis of $W(pic)_4$ can be carried out over a much more diverse range of reaction conditions. The $Mo(pic)_4$ complex has been characterized and its chemistry is compared to that of the $W(pic)_4$ complex and other early transition metal eight-coordinate complexes.

Experimental Section

Synthesis of Tetrakis(picolinato)molybdenum(IV). Molybdenum hexacarbonyl (Pressure Chemical) was purified by vacuum sublimation at 100 °C and stored over potassium hydroxide prior to use. Mesitylene (Eastman) and picolinic acid (Eastman) were used without further purification.

(a) Picolinic acid (3.70 g, 30.0 mmol) and molybdenum hexacarbonyl (0.79 g, 3.00 mmol) were placed in a long-necked 50-mL round-bottom flask with a magnetic stirrer bar. After purging the system with prepurified nitrogen, the flask was immersed in an oil bath at 150 °C. The formation of a dark brown solution began concurrently with the melting of the picolinic acid. No further color changes were observed. The crude product was subjected to vacuum sublimation at 150 °C for 4 h. This treatment removed most of the unreacted $Mo(CO)_6$ and picolinic acid. The complex was then dissolved in methylene chloride, the solution filtered, and hexane added to the filtrate to cause precipitation of $Mo(pic)_4$. The complex was dried in vacuo over potassium hydroxide for 24 h.

Anal. Calcd for $Mo(C_6H_4NO_2)_4$: C, 49.23; H, 2.76; N, 9.59. Found: C, 49.01; H, 3.21; N, 9.06. Yield ≥70%.

(b) Picolinic acid and molybdenum hexacarbonyl (in a 5:1 mole ratio) were allowed to react in mesitylene under reflux conditions and a nitrogen atmosphere for 4 h. After flash evaporation of the solvent, the workup of the complex was identical with (a). Yield ≥70%.

Characterization of Tetrakis(picolinato)molybdenum(IV). (1) Electronic Spectrum. The electronic spectrum of the complex was recorded from 10 000 to 40 000 cm^{-1} on a Hatachi Model EPS-3T spectrophotometer at room temperature. Matched Suprasil cells of 1.000-cm path length were employed in the double-beam measurements. The reference cell contained the same solvent as the sample solution.

(2) Magnetic Susceptibility Measurements. The Faraday method was used for determining the magnetic susceptibility of the complex. $CoHg(SCN)_4$ was used to calibrate the balance. Sample size was ca. 5 mg. The diamagnetism of the ligand was corrected for using Pascal's constant summation method.

(3) Proton Nuclear Magnetic Resonance Spectrum. The ^1H NMR spectrum of the complex was measured on a 90-MHz Perkin-Elmer R32 nuclear magnetic resonance spectrometer. The spectrum was referenced against tetramethylsilane. The reported temperature is accurate to ±2 °C.

(4) Infrared Spectrum. The infrared spectrum was recorded on the Perkin-Elmer 180 spectrometer. The sample was run as a KBr disk vs. air.

Results and Discussion

Whereas Dorsett and Walton[2] report that the reaction of $Mo(CO)_6$ and picolinic acid (1:4 mole ratio) in refluxing methanol or acetonitrile yields only the tris(picolinato)molybdenum(III) complex, we have obtained $Mo(pic)_4$ in high yields, by running the reaction at a higher temperature and by increasing the ligand to $Mo(CO)_6$ mole ratio. The $Mo(pic)_3$ complex is paramagnetic, $\mu_{eff} = 3.74\ \mu_B$, and is susceptible to rapid oxidation in air.[2] The diamagnetic $Mo(pic)_4$ complex ($\chi_g = -0.15 \times 10^{-6}$ cgsu, $\chi_m = -90 \times 10^{-6}$, $\chi_m{}^{cor} = 150 \times 10^6$ at 23 °C) has a $\mu_{eff} = 0.6\ \mu_B$ (zero within experimental error). The slight paramagnetism of the complex may be due to temperature-independent paramagnetism and/or trace amounts of paramagnetic impurities.

While the purple $W(pic)_4$ complex persists in aqueous solution for months,[1] the $Mo(pic)_4$ complex is hydrolyzed within a day. The infrared spectrum of $Mo(pic)_4$, like $W(pic)_4$, is dominated by the $\nu(COO)_{as}$ band at 1674 cm^{-1}. In addition, the spectrum is free of any bands logically assignable to Mo–CO, Mo–O, or Mo–OH units.

The visible spectrum of $Mo(pic)_4$ in $CHCl_3$ is dominated by moderately intense absorption bands at 20 500 cm^{-1} (ϵ 5500) and a weaker band at 27 800 cm^{-1} (ϵ 2000). A maxima at 37 900 cm^{-1} (ϵ 16 000) and a shoulder at 36 500 cm^{-1} (ϵ 13 000) are assigned as $\pi \rightarrow \pi^*$ transitions of the ligand. The low-energy transition of the $Mo(pic)_4$ complex can be assigned as a M → L charge-transfer transition on the basis of its intensity and the shift to lower energy on going from $Mo(pic)_4$ to the more easily oxidizable $W(pic)_4$ complex, for which M → L charge transfer has been shown previously.[1] Analogous to $W(pic)_4$, the low-energy band of $Mo(pic)_4$ exhibits shifts to higher energy in more polar and/or protic solvents: CH_3COOH (21 800 cm^{-1}), H_2O (22 300 cm^{-1}). The 90-MHz ^1H NMR spectrum of $Mo(pic)_4$ in CD_2Cl_2 at 35 °C consists of a poorly resolved doublet at 9.84 ppm (downfield from Me_4Si) and a multiplet centered at 7.71 ppm. The doublet is assigned to the proton α to the pyridine nitrogen, while the remaining aromatic protons cause the multiplet. The ^1H NMR spectrum of the $W(pic)_4$ complex exhibits the same pattern.[1]

Attempts to oxidize $Mo(pic)_4$ to the d^1 $Mo(pic)_4^+$ cation with either Cl_2 or Br_2 for up to several hours yielded only unreacted $Mo(pic)_4$. Such oxidations can be accomplished for the $W(pic)_4$[1] and $W(q_4)$[3] complexes, where q^- = 8-quinolinolato. A variety of substituted dithiocarbamato eight-coordinate molybdenum(IV) complexes have also been successfully oxidized to molybdenum(V) eight-coordinate cations by not only Cl_2 and Br_2 but also I_2.[4] After one attempt to oxidize the $Mo(pic)_4$ complex with a Cl_2/CCl_4 solution, the recovered complex after standing in a capped vial for over a week was observed to have turned blue. The infrared spectrum of this product has five bands between 960 and 860 cm^{-1}, consistent with the formation of a molybdenum–oxo complex.

The single-crystal x-ray structure determination of the tetrakis(5-bromo-8-quinolinolato)tungsten(IV) complex revealed it possesses D_{2d} dodecahedral geometry.[5] The ligands span the *m* edges with the π-acceptor nitrogen atoms occupying the B sites and the π-donor phenolic oxygens occupying the A sites in accordance with Orgel's rule.[6] Given the chemical similarities between 8-quinolinol and picolinic acid, as well as their nearly equal bite sizes, it is assumed the $W(pic)_4$ and $Mo(pic)_4$ complexes also possess D_{2d} (*mmmm*) dodecahedral geometry.

Only a handful of bidentate ligands have been reported to yield tetrakis eight-coordinate molybdenum(IV) complexes. These ligands include CO_3^{2-},[7] $C_2O_4^{2-}$,[8] S_2CR^-,[9] $S_2CNR_2^-$,[4,10] and $(SCC_6H_5)_2CH^-$.[11,12] In addition, no concrete structural evidence is available for the molybdenum(IV) complexes reported for the CO_3^{2-} and $C_2O_4^{2-}$ ligands.

The present results suggest more drastic reaction conditions are necessary to synthesize eight-coordinate molybdenum(IV) complexes than the analogous tungsten(IV) complexes, when oxidation, as well as substitution, is occurring at the metal center. This trend is consistent with the relative oxidation-state stabilities of molybdenum and tungsten. In general, tungsten favors higher oxidation states.

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Registry No. $Mo(pic)_4$, 66008-11-5; $Mo(CO)_6$, 13939-06-5.

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A Direct One-Step Preparation of Bis(dinitrogen) Complexes of Molybdenum(0) from Molybdenum(V) Chloride

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Bis(dinitrogen) complexes of molybdenum(0) have found extensive use in the study of the chemistry of the coordinated dinitrogen ligand, with possible relevance to nitrogenase enzyme systems.[2] The complexes studied generally contain organophosphines as coligands, most notably 1,2-bis(diphenylphosphino)ethane (DPPE), and several schemes have been developed for their synthesis. Hidai et al. were the first to report dinitrogenmolybdenum(0) complexes,[3] the synthesis of which involved the triethylaluminum reduction of molybdenum(III) acetylacetonate in the presence of the appropriate phosphine and under a N_2 atmosphere. The reaction schemes used required several days for completion and only small yields of product were obtained. Chatt and co-workers have employed the magnesium metal or sodium amalgam reduction of $MoCl_3(THF)_3$ in the presence of organophosphines and under N_2.[4] The molybdenum(III) reactant is itself prepared in several steps from $[MoCl_5]_2$. Aresta and Sacco have described the synthesis of $[Mo(N_2)_2L_4]$ complexes (L = monodentate phosphine) from the sodium powder reduction of $[MoCl_4L_2]$.[5] George and Seibold previously reported obtaining $[Mo(N_2)_2L_4]$ and $[Mo(N_2)_2L'_2]$ complexes (L′ = bidentate phosphine) from the sodium amalgam reduction of $[MoCl_4L_2]$ and $[MoCl_4L']$, the molybdenum(IV) reactants having been prepared from $[MoCl_5]_2$.[6] The present note deals with the direct synthesis from $[MoCl_5]_2$ in good yields of complexes of the type $[Mo(N_2)_2L_4]$ and $[Mo(N_2)_2L'_2]$, where L = Ph_2PCH_3 and L′ = DPPE, 1,2-bis(diethylphosphino)ethane (DEPE), and 1-diphenylarsino-2-diphenylphosphinoethane (ARPHOS).

Experimental Section

All solvents were reagent grade and were dried, distilled, and deaerated under dinitrogen prior to use, using the following drying agents during distillation: THF, sodium benzophenone; benzene, calcium hydride; methanol, magnesium methoxide. Molybdenum pentachloride and DPPE were used as obtained from Research Organic/Inorganic Chemicals, Inc. ARPHOS and Ph_2PCH_3 were used as obtained from Pressure Chemical Co. and Strem Chemicals, Inc., respectively. DEPE, from OrgMet, Inc., was purified by vacuum distillation before use. Operations were conducted in a glovebag under a dinitrogen atmosphere. Product identification was based on the characteristic infrared spectra of the compounds as obtained on a Perkin-Elmer Model 621 spectrophotometer as KBr disks. Nitrogen content was determined by the measurement of the gas evolved by thermal or a combination of thermal and bromine decomposition.

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