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Transition-Metal Eight-Coordination. 17. Synthesis and Characterization of Homo- and Heteroligand Tetrakis Molybdenum(IV) Chelates[1]

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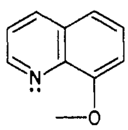
A versatile, specific synthetic route is provided for the isolation of mixed-ligand $MoL_nL'_{4-n}$, where L^- and L'^- are anionic bidentate ligands such as an 8-quinolinolate derivative or the picolinate anion. Isomers of $MoL_2L'_2$ type species have been observed, too. These deeply colored, diamagnetic chelates possess metal-to-ligand charge-transfer transitions in the visible region and exhibit disproportionation reactions at room temperature, even in the solid state. Thermal degradation involves oxygen abstraction from the quinolinol entities in some of the mixed-ligand chelates.

Introduction

Specific synthetic routes to mixed-ligand eight-coordinate chelates of the group 6 metals have been nonexistent even though a full series of $WL_nL'_{4-n}$ chelates have been isolated, where L^- and L'^- are anionic nitrogen/oxygen donors of the 8-quinolinolate (**1**) and picolinate (**2**) types, respectively.[3] The high-temperature reaction used to prepare these species (eq 1), where 1 mol of ligand is reduced to the tetrahydro derivative, as shown earlier,[4] precludes kinetic control of individual products. Thus, chromatographic separation of the individual species was required. Furthermore, attempts to prepare analogous molybdenum chelates with molybdenum carbonyl and 8-quinolinol derivatives invariably produced tars, regardless of the specific procedures attempted.[5]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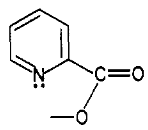
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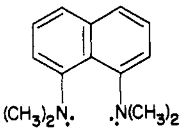
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$$W(CO)_6 + 5(HL + HL') \rightarrow WL_nL'_{4-n} + (HLH_4 + HL'H_4) + 6CO \quad (1)$$

Simple substitution reactions of such bidentate ligands (HL) with $MoCl_4$ usually stop at the $MoCl_2L_2$ stage[6] because of insolubility, although $MoClL_3$ complexes have been obtained at elevated temperatures with appropriate solvents.[7] Sulfur donor $MoCl(S-S)_3$ species, where S–S represents a dithio acid or a dithiocarbamate anionic ligand, have also been obtained by others,[8] either by indirect means or by accident, and the $Mo(S-S)_4$ donor set is quite common.[9] Using Proton Sponge, **3**, we are able to completely substitute oxygen/nitrogen donor bidentate ligands for the chlorides of $MoCl_4$ and make specific mixed-ligand complexes by design rather than by chance.

Experimental Section

Solvents, Reagents, and Precursors. Carbon tetrachloride, hexane, methanol, methylene chloride, and toluene were all dried and deoxygenated by heating under reflux conditions for 4 h over calcium hydride followed by distillation from calcium hydride under prepurified nitrogen gas. Spectroanalyzed chloroform was deoxygenated by bubbling prepurified nitrogen through the solvent immediately prior to use.

Proton Sponge, Aldrich's trade name for 1,8-bis(dimethylamino)naphthalene, was used without further purification.

Ligands were sublimed (at the temperatures indicated) prior to their use in this study: 5,7-dichloro-8-quinolinol, 150 °C; 5,7-dibromo-8-quinolinol, 150 °C; 5-nitro-8-quinolinol, 150 °C; 5-chloro-8-quinolinol, 110 °C; picolinic acid, 110 °C; 8-quinolinol, 80 °C. Purity was confirmed by chemical analyses and melting points.

The chloromolybdenum chelate reagents dichlorobis(5-chloro-8-quinolinolato)molybdenum(IV), dichlorobis(5,7-dichloro-8-quinolinolato)molybdenum(IV), chlorotris(picolinato)molybdenum(IV), chlorotris(5,7-dibromo-8-quinolinolato)molybdenum(IV), and chlorotris(5,7-dichloro-8-quinolinolato)molybdenum(IV) were prepared as described previously.[7]

Syntheses. Although neither the reactants nor the products of the synthetic reactions are particularly air sensitive, solutions of both are quite sensitive to moist air. Therefore, all reactions were performed under an atmosphere of prepurified nitrogen or argon by using standard drybox/drybag or Schlenk techniques.

Tetrakis(5,7-dichloro-8-quinolinolato)molybdenum(IV), Mo(dcq)$_4$. In a typical reaction, 0.40 g (0.52 mmol) of chlorotris(5,7-dichloro-8-quinolinolato)molybdenum(IV), 0.11 g (0.52 mmol) of 5,7-dichloro-8-quinolinol, and 0.11 g (0.52 mmol) of Proton Sponge were added to 30 mL of 9:1 v/v methylene chloride/methanol. The resulting blue solution was stirred for 20 min and filtered. The red-purple precipitate was washed with three 5-mL portions of the 9:1 methylene chloride/methanol solvent and dried in vacuo for 24 h at 150 °C; yield 0.39 g (79%).

Thin-layer chromatography of this compound has one blue spot at R_f 0.95. The microcrystalline product is red-violet by reflected light in the bulk solid, and very thin crystals appear blue by transmitted light under a microscope at 400×. Thicker crystals appear opaque.

Anal. Calcd for $MoC_{36}H_{16}N_4O_4Cl_8$: C, 45.60; H, 1.70; N, 5.91; Cl, 29.92. Found: C, 45.50; H, 1.80; N, 5.72; Cl, 30.09.

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[1] Presented in part of the Fourth International Conference on the Chemistry and Uses of Molybdenum, Golden, CO, 1982, and in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, 1982. Taken in part from: Weber, C. J. Ph.D. Dissertation, University of Massachusetts, 1981.

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Tetrakis(5,7-dibromo-8-quinolinolato)molybdenum(IV), $Mo(dbq)_4$. First, 0.09 g (0.29 mmol) of 5,7-dibromo-8-quinolinol and 0.06 g (0.29 mmol) of Proton Sponge were dissolved in 7 mL of 9:1 v/v methylene chloride/methanol. To this solution was added 0.30 g (0.29 mmol) of chlorotris(5,7-dibromo-8-quinolinolato)molybdenum(IV). The resulting dark blue solution was stirred for 20 min. The purple solid was then filtered from the solution, washed with two 3-mL portions of the 9:1 methylene chloride/methanol, and dried 12 h in vacuo at 150 °C; yield 0.20 g (53%).

Thin-layer chromatography of this product gives a single blue spot at R_f 0.95.

Anal. Calcd for $MoC_{36}H_{16}N_4O_4Br_8$: C, 33.16; H, 1.24; N, 4.30; Br, 49.03. Found: C, 33.09; H, 1.33; N, 4.36; Br, 48.84.

Tris(5,7-dichloro-8-quinolinolato)(picolinato)molybdenum(IV), $Mo(dcq)_3(pic)$. First, 0.40 g (0.52 mmol) of chlorotris(5,7-dichloro-8-quinolinolato)molybdenum(IV), 0.07 g (0.57 mmol) of picolinic acid, and 0.12 g (0.57 mmol) of Proton Sponge were added to 15 mL of 9:1 v/v methylene chloride/methanol. The solution, which rapidly turned purple, was stirred for 20 min and then allowed to evaporate down to 5 mL under gentle heating. Filtration gave a red solid, which was washed with three 5-mL portions of methanol. The dark red product was dried in vacuo at 100 °C for 4 days; yield 0.2 g (50%).

Thin-layer chromatography of this complex shows an intense violet spot at R_f 0.81. This spot turns brown very rapidly. A very faint blue spot at R_f 0.97 and another very faint red spot at R_f 0.44 were also observed. Very thin crystals of this compound appear red-violet to transmitted light under a microscope at 400×.

Anal. Calcd for $MoC_{33}H_{16}N_4O_5Cl_6$: C, 46.23; H, 1.88; N, 6.54; Cl, 24.81. Found: C, 46.10; H, 2.15; N, 6.22; Cl, 25.08.

Tris(5,7-dichloro-8-quinolinolato)(5-nitro-8-quinolinolato)molybdenum(IV), $Mo(dcq)_3(nq)$. First, 0.50 g (0.65 mmol) of chlorotris(5,7-dichloro-8-quinolinolato)molybdenum(IV), 0.13 g (0.65 mmol) of 5-nitro-8-quinolinol, and 0.14 g (0.65 mmol) of Proton Sponge were added to 7 mL of 1:1 v/v methylene chloride/methanol. The resulting blue-green solution was stirred for 15 min and filtered. The red-purple precipitate was dissolved in 15 mL of hot carbon tetrachloride and filtered. The volume of this solution was reduced to 8 mL, the solution was allowed to cool to room temperature, and 3 mL of hexane was added slowly. The solution was allowed to sit for 24 h and was filtered, giving a dark, microcrystalline product that was washed with two 3-mL portions of hexane. It was dried in vacuo for 15 h at 150 °C; yield 0.41 g (68%).

Thin-layer chromatography of this complex using a 50:1 chloroform/methanol mixture as the eluent gives an intense turquoise blue spot at R_f 0.85, a faint blue spot at about R_f 0.98, and an even fainter green spot at R_f 0.75. Thin crystals of this compound appear turquoise blue to transmitted light under a microscope at 400×.

Anal. Calcd for $MoC_{36}H_{17}N_5O_6Cl_6$: C, 46.78; H, 1.85; N, 7.58; Cl, 23.02. Found: C, 46.74; H, 1.91; N, 7.50; Cl, 23.30.

Bis(5,7-dichloro-8-quinolinolato)bis(picolinato)molybdenum(IV), $Mo(dcq)_2(pic)_2$. Initially, 0.300 g (0.50 mmol) of dichlorobis(5,7-dichloro-8-quinolinolato)molybdenum(IV), 0.123 g (1.00 mmol) of picolinic acid, and 0.215 g (1.00 mmol) of Proton Sponge were added to 7 mL of 9:1 v/v methylene chloride/methanol. The slurry was placed in a sealed flask and stirred for 1 h at 0 °C. The solvent was removed under vacuum, and the red residue was dissolved in 80 mL of methylene chloride. The volume of the solution was reduced to 15 mL, and then 10 mL of hexane was slowly added to precipitate the Proton Sponge salt, which was filtered from the solution. The addition of 25 mL more of hexane caused precipitation of the product, which then was filtered, washed with hexane, and dried at 150 °C for 15 h; yield 0.23 g (63%).

Thin-layer chromatography of this complex gives a red spot at R_f 0.30. Very thin crystals of this compound appear red-violet to transmitted light under a microscope at 400×.

Anal. Calcd for $MoC_{30}H_{16}N_4O_6Cl_4$: C, 47.02; H, 2.10; N, 7.31; Cl, 18.50. Found: C, 47.12; H, 2.23; N, 7.05; Cl, 18.18.

Bis(5,7-dichloro-8-quinolinolato)bis(5-nitro-8-quinolinolato)molybdenum(IV). First, 0.300 g (0.50 mmol) of dichlorobis(5,7-dichloro-8-quinolinolato)molybdenum(IV), 0.191 g (1.00 mmol) of 5-nitro-8-quinolinol, and 0.215 g (1.00 mmol) of Proton Sponge were added to 7 mL of 9:1 v/v methylene chloride/methanol. The slurry was placed in a sealed flask and stirred 1 h at 0 °C. The solution was filtered, and the purple precipitate was washed with methanol and dried at 150 °C for 15 h; yield 0.30 g (66%).

Thin-layer chromatography with 50:1 v/v chloroform/methanol as the eluent gives two blue-green spots at R_f 0.91 and 0.78. The spot at 0.91 has greater intensity. Under a microscope at 400×, the material appears purple to reflected light and blue-green to transmitted light.

Anal. Calcd for $MoC_{36}H_{18}N_6O_8Cl_4$: C, 48.02; H, 2.02; N, 9.34; Cl, 15.75. Found: C, 48.00; H, 1.88; N, 9.05; Cl, 16.06.

Characterization Methods. Infrared spectra of all synthesized complexes were recorded on a Beckman IR-10 spectrophotometer. The electronic reflectance and absorbance spectra were recorded on a Cary 14 spectrophotometer. Magnetic susceptibility measurements were obtained by the Faraday method using a Cahn automatic electrobalance and an Alfa electromagnet. $Hg[Co(NCS)_4]$ was used as a calibration standard. Corrections were made for paramagnetism in the sample dish and for the diamagnetism of the ligands. Thermogravimetric analyses under a helium atmosphere were performed with a Du Pont 950 thermogravimetric analyzer controlled by a Du Pont 900 thermal analyzer at a heating rate of 10 °C/min.

Products were chromatographed by thin-layer chromatography (TLC) on Redi/Plates (Analtech), which consist of glass plates coated with 250 μm of Silica Gel G. The plates were activated for 1 h at 100 °C prior to use. The eluent was a mixture of 30 parts of chloroform to 1 part methanol (v/v), except where another eluent is specified. R_f determinations are an average of at least two values.

Elemental analyses were obtained from the University of Massachusetts Microanalytical Laboratory.

Results and Discussion

Reactions 2 and 3 provide convenient routes to both hetero- and homoligand chelates of eight-coordinate molybdenum(IV),

$$MoCl_2L_2 + 2HL' + 2PS \rightarrow MoL_2L'_2 + 2PSH^+Cl^- \quad (2)$$

$$MoClL_3 + HL' + PS \rightarrow MoL_3L' + PSH^+Cl^- \quad (3)$$

where HL and HL′ may be the same or different derivatives of 8-quinolinol or picolinic acid and PS = Proton Sponge. While van den Bergen, Murray, and West[6c] reported that preliminary attempts to convert chloromolybdenum chelates to eight-coordinate chelates had failed, we have observed that the chloro chelates are converted to eight-coordinate complexes by reaction in a solvent of moderate polarity with a quinolinol or picolinic acid derivative *in the presence of a noncoordinating base*. Both the presence of the base and the polarity of the solvent are important factors in these reactions. The attempted reaction of $Mo(dcq)_3Cl$ and Hpic even at high temperatures, but in the absence of base, resulted only in replacement of dcq^- with pic^-. The desired reaction does not occur even in the presence of a base such as Proton Sponge [1,8-bis(dimethylamino)naphthalene] in a solvent of low polarity such as CH_2Cl_2 or toluene. A mixed-solvent system consisting of 10% methanol and 90% CH_2Cl_2 (v/v) is adequate for proton transfer, though hydrogen bonding rather than polarity could be the critical factor.

The base Proton Sponge was used as a deprotonating agent, because although it is a relatively strong proton acceptor ($pK_a \sim 12.3$),[10] the presence of the methyl groups around the amines make it a very poor nucleophile for large transition-metal ions. Therefore, it does not compete for the coordination sites on molybdenum.

The syntheses of $Mo(dcq)_4$ from $Mo(dcq)_3Cl$ and $Mo(dbq)_4$ from $Mo(dbq)_3Cl$ provide high yields. These reactions are probably quantitative, but the solubility of the products in the reaction solvent decreases the amount of recovered products.

In contrast, the TLC's of $Mo(dcq)_3(pic)$ and $Mo(dcq)_3(nq)$ indicate that the reactions of $Mo(dcq)_3Cl$ designed to give mixed-ligand complexes often result in a trace of ligand scrambling. The faint blue spots at R_f 0.97–0.98 are identified as $Mo(dcq)_4$ on the basis of color and R_f. The faint red spot at R_f 0.44 and the faint green spot at R_f 0.75 are identified

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(10) Alder, R. W.; Bowman, P. S.; Steele, W. R. P.; Wintermann, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 723.

as 2:2 chelates of dcq⁻ and pic⁻ or nq⁻, respectively.

The intensities of these spots resulting from ligand scrambling are very low relative to the major spot in both of these reactions, and we estimate that the scrambling products are approximately 1% of the total product. Extinction coefficients of $\sim 10^4$ make even traces visible on the TLC plates.

The syntheses of $Mo(AB)_2(A'B')_2$ complexes were conducted at 0 °C in order to minimize the amount of scrambling. Longer reaction times were required for complete reaction of the relatively insoluble dichloro starting materials. No ligand scrambling products were observed in fresh complexes. However, thin-layer chromatograms of samples that had been at room temperature for 1 month showed that some ligand scrambling had occurred in the solid state over this period. In a sample of $Mo(dcq)_2(pic)_2$ both $Mo(dcq)_3(pic)$ and $Mo(dcq)(pic)_3$ as well as traces of $Mo(dcq)_4$ and $Mo(pic)_4$ were observed.

The reaction of $Mo(pic)_3Cl$ with Hdcq results in a number of products. It is interesting that the major products of this reaction are $Mo(dcq)_2(pic)_2$ and $Mo(pic)_4$. Apparently $Mo(pic)_3Cl$ decomposes rapidly in polar solvents. A chromatogram of a brown solution of "$Mo(pic)_3Cl$" in a polar solvent has as its major component $Mo(pic)_4$. A byproduct of this decomposition reaction might be a $Mo(pic)_2Cl_2$ species that could then react with Hdcq to give $Mo(dcq)_2(pic)_2$. Traces of both $Mo(dcq)_3(pic)$ and $Mo(dcq)_4$ are observed in the chromatogram of the $Mo(pic)_3Cl$–Hdcq reaction products. These $Mo(dcq)_n(pic)_{4-n}$ complexes must be slightly labile since $Mo(dcq)_4$ will only be formed by a stepwise replacement of pic⁻ ligands by dcq⁻ ligands in these complexes.

The ligand field d-orbital schemes for eight-coordination have one low-lying d-like orbital. Thus, a complex with a d^2 electronic configuration in either of these two common eight-coordinate geometries should be substitution inert.[11] Such inertness has been observed for tungsten eight-coordinate complexes.[3,4,12] Apparently in $Mo(dcq)_n(pic)_{4-n}$ complexes this stabilization is not sufficient to compensate for the poor donor ability of the picolinato ligand as some displacement of pic⁻ with dcq⁻ occurs at room temperature—even in the solid state.

The synthesis of the parent 8-quinolinol complex $Mo(q)_4$ was also accomplished, but the purity of the resulting blue complex was poor. Its solubility in solvents in which it does not decompose is too low for purification. The electronic and infrared spectra are consistent with an eight-coordinate chelate in this case, too. It proved to be the least stable of all of the complexes synthesized in this study. It decomposes slowly at room temperature in a sealed vial. The compound was also synthesized in an impure state earlier by Bradley[13] by metathesis between $Mo[N(CH_3)_2]_4$ and Hq.

The lability of these complexes is evident from Figure 1, which schematically shows the products of the elevated-temperature reaction between $Mo(dcq)_3Cl$ and Hpic (in the presence of Proton Sponge) as a function of time. Chromatograms used to follow the changing product ratios provide evidence for some scrambling almost immediately and a complete scrambling after only 85 min at 50 °C. The molybdenum-containing products [with colors and R_f values in brackets] are as follows: $Mo(dcq)_4$ [blue, 0.96]; $Mo(dcq)_3(pic)$ [purple, 0.68]; α-$Mo(dcq)_2(pic)_2$ [faint grayish, 0.44]; β-$Mo(dcq)_2(pic)_2$ [red, 0.32]; $Mo(dcq)(pic)_3$ [faint orange, 0.23]; $Mo(pic)_4$ [yellow-brown, 0.06]. Assignments for most of the species were made from authentic samples, and for the remainder, assignments were made by comparison with analogous $W(dcq)_n(mpic)_{4-n}$ species,[3] where mpic⁻ = 5-methylpicolinate. The R_f values of the molybdenum chelates are very similar to the analogous tungsten complex with the same eluant. This observation, together with the virtually identical size of the two parent metal ions, suggests that the molybdenum chelates are isostructural with the tungsten chelates, for which structural evidence of eight-coordination is available.[11]

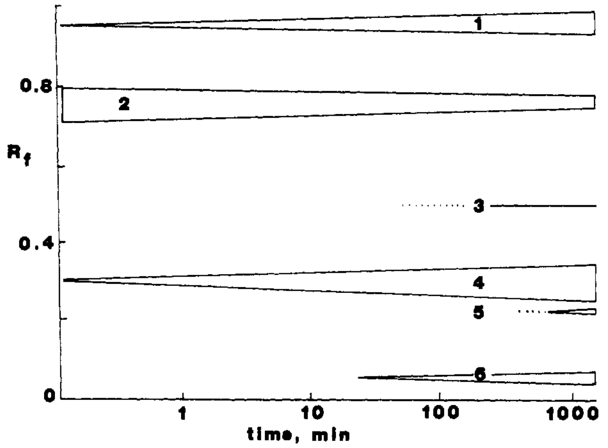

Figure 1. Thin-layer chromatograms of the molybdenum-containing reaction products between $Mo(dcq)_3Cl$, Hpic, and Proton Sponge (1:1:1 molar ratio) as a function of time. Spot assignments: 1, $Mo(dcq)_4$; 2, $Mo(dcq)_3(pic)$; 3, α-$Mo(dcq)_2(pic)_2$; 4, β-$Mo(dcq)_2(pic)_2$; 5, $Mo(dcq)(pic)_3$; 6, $Mo(pic)_4$.

Thin-layer chromatograms of the synthetic 2:2 chelates provide evidence for geometric isomers in the case of $Mo(dcq)_2(nq)_2$, but not for $Mo(dcq)_2(pic)_2$. On the other hand, a trace of the second $Mo(dcq)_2(pic)_2$ isomer appears in the long-term elevated-temperature reaction noted above. No evidence for silica gel induced isomerization could be obtained in either case, unlike the analogous $W(dcq)_2(mpic)_2$ isomers, which isomerize readily on silica gel, even though their solution isomerization has a high activation energy.[3] The ease of substitution on molybdenum relative to tungsten in these eight-coordinate species might make this lack of isomerization seem paradoxical, but the tungsten isomerization was deemed to be a twist process, not necessarily any more accessible to molybdenum. In fact, the greater lability of the molybdenum complexes suggests decomposition may occur during any twist reactions with the molybdenum species. Brown byproduct spots are found on some of the chromatograms.

The TLC spots vary in their stability to air and light and $Mo(dcq)_4 >$ β-$Mo(dcq)_2(pic)_2 \sim Mo(pic)_4 > Mo(dcq)_3(pic) \sim Mo(dcq)(pic)_3 \geq$ α-$Mo(dcq)_2(pic)_2$. Also, $Mo(dbq)_4 > Mo(dcq)_4 > Mo(pic)_4 > Mo(q)_4$. The lack of appreciable amounts of the α isomer may be kinetically controlled either in the synthesis or by decomposition on the TLC plates. In the tungsten series the α isomer is more stable thermodynamically than the β one by a factor of 4:1 at room temperature,[3] and it is difficult to see why the molybdenum series would be different. However, ligand activation energies can vary relative to the isomer and ligand position, if nonequivalent positions exist. Possibly the α isomer labilizes the ligands. The relative stabilities of the MoL_4 species are logical from the close proximity of the oxygen atoms (~2.4 Å) in the tungsten chelate for which structural data are available[11] and from the nucleophilicity of the ligands toward metals. The electron-withdrawing tendencies of the chloro and nitro groups stabilize the dcq⁻ and nq⁻ derivatives relative to q⁻ by removing electron

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(11) This concept is discussed in detail in: Bonds, W. D.; Jr.; Archer, R. D.; Hamilton, W. C. *Inorg. Chem.* **1971**, *10*, 1764.

(12) (a) Archer, R. D.; Bonds, W. D., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 2236. (b) Bonds, W. D., Jr.; Archer, R. D. *Inorg. Chem.* **1971**, *10*, 2057. (c) Archer, R. D.; Donahue, C. J.; Batschelet, W. H.; Whitcomb, D. R. In "Inorganic Compounds with Unusual Properties II"; King, R. B., Ed.; American Chemical Society: Washington, DC, 1979; Adv. Chem. Ser. No. 173, p 252. (d) Donahue, C. J.; Archer, R. D. *Inorg. Chem.* **1977**, *16*, 2903.

(13) Bradley, D. C., private communication.

Table I. Solution Spectra of Several Eight-Coordinate Molybdenum Complexes in CCl_4[a]

$Mo(dcq)_4$[b]	$Mo(dbq)_4$[b]	$Mo(dcq)_3(q)$[b]	$Mo(dcq)_3(pic)$[c]	$Mo(dcq)_3(nq)$[d]
				15.6 (8.7) sh
16.7 (39.0)	16.6 (29.0)	16.7 (33.0)	17.2 (22.0)	16.7 (21.0)
18.2 (23.0) sh	18.0 (18.0)	18.2 (20.0) sh	18.3 (15.0) sh	18.2 (11.0) sh
	19.6 (7.3) sh			19.6 (6.3) sh
24.3 (13.0)	24.3 (10.0)	24.3 (11.0)		23.9 (11.0)
25.3 (13.0)	25.2 (10.0)	25.2 (11.0)	25.9 (7.2)	24.7 (11.0)
27.0 (12.0) sh	26.7 (8.7) sh	27.0 (9.4) sh	26.9 (6.9) sh	26.8 (9.7) sh
31.1 (9.0)	31.0 (8.0)	31.8 (8.0)	31.2 (5.4) sh	31.1 (8.7) sh
32.3 (9.0)	32.4 (8.7)		32.8 (5.4) sh	32.1 (8.7)

[a] Energies are reported in $cm^{-1} \times 10^3$. The number in parentheses is 10^{-3} times the molar extinction coefficient. [b] Blue-blue-violet solution. [c] Red-red-violet solution. [d] Turquoise blue solution.

Table II. Reflectance Spectra of Several Eight-Coordinate Molybdenum Complexes in Nujol[a]

$Mo(dcq)_4$[b]	$Mo(dbq)_4$[b]	$Mo(q)_4$[c]	$Mo(dcq)_3(q)$[b]	$Mo(dcq)_3(pic)$[d]	$Mo(dcq)_3(nq)$[c]
					15.4
16.3	16.4	16.0	16.4	17.0	16.4
17.9 sh	17.9 sh	17.4 sh	17.9 sh	18.2 sh	17.9 sh
19.6 sh	19.6 sh			20.0 sh	19.6 sh
24.3	23.9		24.1	24.7 sh	23.9
25.1	25.0	25.6	25.2	25.6	
			27.0	27.0	

[a] Energies are reported in $cm^{-1} \times 10^3$. [b] Red-violet solid. [c] Dark blue. [d] Red.

density from the overcrowded oxygen donors. The lower nucleophilicity of the pic^- ligand is evident from its position in the stability series, although its more ready oxidation may also be responsible. The oxidation tendencies undoubtedly have an effect on the quinolinol derivatives, too.

Spectra. The infrared spectra of the quinolinolate-containing complexes all show the characteristic quinoline pattern of four strong bands at about 1550, 1490, 1450, and 1360 cm^{-1}. The picolinate-containing complexes exhibit a strong band ($\sim$1670–1680 cm^{-1}) assigned as a carbonyl stretch. The 940-cm^{-1} region can be used to find oxidized products (terminal Mo=O stretch), although a weak band exists in this region in some of the ligands.

Absorption and reflectance electronic spectra of these molybdenum chelates all contain two intense bands in the visible region and are qualitatively similar to those observed in analogous tungsten complexes. The low-energy band has at least three components (i.e., two shoulders) in $Mo(dcq)_4$ and shifts to higher energy in $Mo(dcq)_n(pic)_{4-n}$ and to lower energy in $Mo(dcq)_n(nq)_{4-n}$. These shifts together with the higher energy of these transitions relative to the tungsten species support the previous assignment[12b] of the major component of this band as a metal-to-ligand charge-transfer transition. The higher energy band at about 400 nm is assigned as intraligand as in the case of the tungsten species. Reflectance spectra exhibit transitions shifted to slightly lower energy (600–1000 cm^{-1}; 10–15 nm) from those in CCl_4 solutions. Compare Tables I and II and Figures 2 and 3. This shift affects the visual colors somewhat, too, as noted in the footnotes of the tables.

Magnetic and Thermal Properties. The complexes are diamagnetic to within experimental error, which is consistent with low-spin eight-coordinate d^2 systems. Both the D_{2d} trigonal-faced dodecahedron and the D_{4d} square antiprism, which are logical ground-state structures, have one low-lying d orbital.[11,14] However, the C_{2v} hendecahedron, or bicapped trigonal prism, cannot be ruled out. Arguments favoring the dodecahedron for these d^2 $M(N-O)_4$ type chelates with a sorting of positions has been noted earlier.[11] The detailed isomer studies with the dodecahedral tungsten complexes[3b] and the analogous chromatographic and spectral results for the molybdenum complexes of this study cause us to lean toward that geometry with the bidentate ligands spanning the trapezoidal *m* edges; cf., ref 3b.

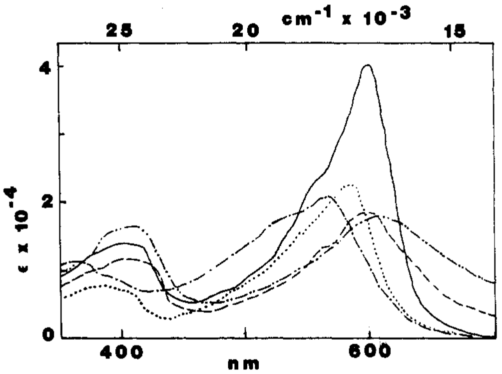

Figure 2. Absorption spectra (CCl_4): (—) $Mo(dcq)_4$; (---) $Mo(dcq)_3(pic)$; (-·-) $Mo(dcq)_2(pic)_2$; (--) $Mo(dcq)_3(nq)$; (-··-) $Mo(dcq)_2(nq)_2$.

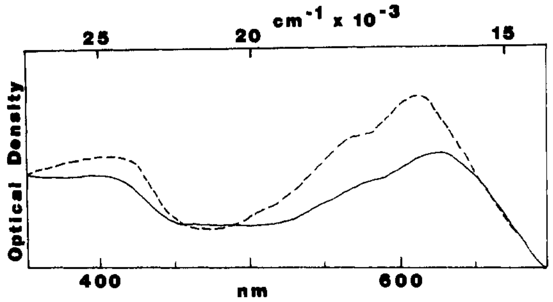

Figure 3. Reflectance spectra: (—) $Mo(dcq)_4$; (---) $Mo(q)_4$.

Thermal gravimetric analyses of several of the complexes indicate the initial loss of quinoline or a quinoline derivative, *not* a quinolinol or a picolinate ligand. Specifically, the first major decomposition occurs at 230 °C for $Mo(dcq)_4$ and $Mo(dbq)_4$, at 220 °C for $Mo(dcq)_3(q)$, at 190 °C for $Mo(dcq)_3(pic)$, and at 180 °C for $Mo(dcq)_3(nq)$, with weight losses of 20%, 16%, 22%, 26%, and 15%, respectively. These values are most consistent with the loss of dichloroquinoline, bromoquinoline, dichloroquinoline, dichloroquinoline, and quinoline fragments, respectively. Oxidation of the metal by

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(14) (a) Pribush, R. A.; Archer, R. D. *Inorg. Chem.* **1974**, *13*, 2556 and references cited therein. (b) Burdett, J. K.; Hoffmann, R.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2553.

an oxygen atom transfer to the metal from the ligand is also consistent with the second weight loss step of a similar magnitude for $Mo(dcq)_4$ at about 350 °C, which would give $MoO_2(dcq)_2$ at the end of the two steps. The loss of dichloroquinoline in the $Mo(dcq)_3(pic)$ complex is interesting and consistent with the stronger metal to oxygen bond in the better nucleophile (dcq^-) and the suggested loss of quinoline derivatives (as opposed to quinolinol derivatives). The weaker donor ability of the carboxylate also indirectly strengthens the metal–oxygen bond of at least one dichloroquinolinolate to the extent that the decomposition temperature is lowered by 40 °C relative to $Mo(dcq)_4$. As noted above, the weight losses for $Mo(dbq)_4$ and $Mo(dcq)_3(nq)$ suggest bromoquinoline and quinoline, respectively. Why or how the dibromoquinoline transfers a bromine or the nitroquinoline transfers a nitro group is pure speculation at this point and needs mass spectral verification. The fate of the quinoline radicals is also unknown for these species.

Conclusions. By the use of anionic eight-coordinate quinolinolate and picolinate donors, complete substitution of the chlorides of $MoCl_4$ occurs and allows the preparation of MoL_4 complexes.[15] Since the neutral ligands only allow partial substitution, specific two-step routes to mixed-ligand eight-coordinate chelates are now possible. Even isomers of the 2:2 complexes have been observed, although they do not appear to undergo the twist isomerization noted for the tungsten analogues; instead, substitution and oxidative decomposition occur. Ligand scrambling is more prevalent in the molybdenum complexes, and decomposition occurs more readily. In fact, some of the tungsten complexes have been prepared at or near the decomposition temperatures of the molybdenum complexes.

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Registry No. $Mo(dcq)_4$, 87739-33-1; $Mo(dbq)_4$, 87854-58-8; $Mo(dcq)_3(pic)$, 88027-25-2; $Mo(dcq)_3(nq)$, 88005-42-9; $Mo(dcq)_2(pic)_2$, 87854-59-9; $Mo(dcq)_2(nq)_2$, 87854-60-2; $Mo(dcq)_3(q)$, 92901-38-7; $Mo(q)_4$, 87854-61-3; $Mo(dcq)(pic)_3$, 74594-59-5; $Mo(pic)_4$, 18307-05-6; $Mo(dcq)_3Cl$, 74620-90-9; $Mo(dbq)_3Cl$, 87739-31-9; $Mo(dcq)_2Cl_2$, 74594-57-3; $Mo(pic)_3Cl$, 87739-32-0.

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[15] We had been able to prepare $Mo(pic)_4$ by the reaction shown as eq 1; cf.: Donahue, C. J.; Archer, R. D. *Inorg. Chem.* **1978**, *17*, 1677. Its properties are consistent with those in this study.

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Substitution Reactions of Five-Coordinate Complexes. 1. Formation and Aquation Kinetics of the (Acido)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (Blue) Cation

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Rate constants for the formation (k_f) and the aquation (k_{aq}) of seven different (acido)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (blue) complexes, $[Cu(tet\ b)Y(blue)]^+$ ($Y^- = Cl^-, Br^-, I^-, SCN^-, N_3^-, O_2CMe^-, CN^-$), have been determined between 15.0 and 40.0 °C at $\mu = 0.10$ M ($NaNO_3 + NaY$) by the stopped-flow method. These complexes present a trigonal-bipyramidal geometry with Y^- or H_2O in equatorial position. The equilibrium constants, K_Y, for the complexation reactions of $[Cu(tet\ b)(H_2O)(blue)]^{2+}$ with these anions obtained by spectrophotometric measurements under equilibrium conditions are in excellent agreement with kinetically determined values (k_f/k_{aq}). A graph of log k_f against log K_Y gives a slope of 0.85. The kinetic results are consistent with an associative-interchange, I_a, mechanism.

Introduction

An examination of substitution in five-coordinated complexes merits attention since they represent an intermediate case, in both a kinetic and steric sense, between the four-coordinated complexes, which are open to nucleophilic attack, and the six-coordinated systems, which are not.[1] Clearly, both associative and dissociative mechanisms are possible, since a five-coordinate complex can potentially either added or lose a unidentate ligand.[2] In order to expand the knowledge in this area, we have initiated a systematic kinetic study of ligand substitution in five-coordinated complexes $[MLX]^{(2-n)+}$ (eq 1), where M is a bivalent metal ion, L is a macrocyclic quadridentate ligand, and X^{n-} and Y^{m-} are unidentate ligands. In this reaction, the four coordination positions are rendered inert by using the strongly complexing macrocyclic ligand, and the unidentate ligand exchanges with each other. Equilibrium constants of some of these reactions have been reported.[3-6]

$$MLX^{(2-n)+} + Y^{m-} \rightleftarrows MLY^{(2-m)+} + X^{n-} \qquad (1)$$

The present paper is concerned with the kinetics of the formation and aquation of (acido)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (blue) complexes, $[Cu(tet\ b)Y(blue)]^+$ ($Y^- = Cl^-, Br^-, I^-, N_3^-, SCN^-, O_2CMe^-, CN^-$), in aqueous solution (eq 2).

$$[Cu(tet\ b)(H_2O)(blue)]^{2+} + Y^- \rightleftarrows [Cu(tet\ b)Y(blue)]^+ + H_2O \quad k_f,\ k_{aq},\ K_Y \quad (2)$$

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