

the reagent. For each of the five substrates the results show that the rates of reaction increase with an increase in the polarizability of the nucleophile. This is in accord with the affinity of a soft base for a soft acid¹⁶ (or class b metal). That the plots of the linear free energy relationships shown in Figure 2 are all approximately parallel indicates that although the various compounds differ in reactivity, they have about the same discriminating ability for the various nucleophiles.

The rate data on the second step of CO substitution presented in Table IV are arranged in order of decreasing reactivity. It is seen that the good π -bonding ligands, e.g., $\text{CNC}_6\text{H}_{11}$ and $\text{P}(\text{OCH}_3)_3$, react more rapidly than the poorer π bonders, e.g., the phosphines. This is reasonable since the good π bonders are

in better competition for the electron density on the metal atom with the two remaining CO's than are the poor π bonders. Thus, the phosphite complexes have weaker M-CO bonds than do the phosphine complexes, and this conclusion is borne out by the infrared spectra of the complexes. Furthermore, in analogy to the ligand-exchange reactions the phosphite derivatives should be more susceptible to CO substitution than the phosphine derivatives, since the phosphites can better stabilize the five-coordinated transition state through stronger π bonding. However, the size of the ligand also seems to be important, since the derivative of $\text{P}(\text{OC}_6\text{H}_5)_3$ which is a good π -bonding ligand but very bulky is very slow to react.

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Complex Compounds of Quadrivalent Molybdenum¹

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A series of complex compounds of molybdenum(IV) of the type $\text{MoBr}_4 \cdot 2\text{L}$ and $\text{MoBr}_4 \cdot \text{B}$ have been prepared, where L is a monodentate ligand and B is 2,2'-dipyridyl. Some of the corresponding molybdenum tetrachloride complexes were also prepared and characterized. Under comparable reaction conditions, reduction of MoBr_4 but not MoCl_4 was observed with pyridine at room temperature and with 2,2'-dipyridyl at elevated temperature. The benzonitrile complexes of MoCl_4 and MoBr_4 appear to be isomorphous as do the complexes obtained with 2,2'-dipyridyl. The visible and ultraviolet spectra of the complexes were examined, in the interest of both characterizing and understanding the nature of chemical bonding between metal and ligand.

Introduction

In recent years many compounds containing molybdenum halides and pseudohalides have been described. Except for the octacoordinate cyanides, $\text{M}_4\text{Mo}(\text{CN})_8$,³ complexes of molybdenum(IV) were relatively unknown until only recently. Other eight-coordinate species which have been described are the triphenylarsine oxide,⁴ the oxalate,⁵ and the carbonate⁵ complexes. Several investigators have recently reported hexahalo molybdate(IV) salts, M_2MoX_6 , as formed under a variety of conditions.⁶⁻¹⁰ The range of M included Na, K, Rb, and Cs, as well as pyridinium

and tertiary ammonium cations, and X may be Cl, Br, or in some cases F.

Starting with molybdenum(V), Fowles and co-workers¹¹ prepared an extensive number of hexacoordinate molybdenum(IV) complexes. The first of these, $\text{MoCl}_4(\text{RCN})_2$, where R is methyl, ethyl, and *n*-propyl, were prepared by the reaction of MoCl_5 with the alkyl cyanide. In later work other complexes such as the tetrahydrofuran, pentamethylene oxide, α -picoline, pyridine, triphenylphosphine oxide, and 2,6-dimethylpyrazine diadducts and the 2,2'-dipyridyl and 1,10-phenanthroline monoadducts were produced by replacement of *n*-propyl cyanide in the complex, $\text{MoCl}_4(\text{C}_3\text{H}_7\text{CN})_2$.¹² Interpretation of the infrared spectra of the monodentate ligand complexes indicated the organic ligands to be in the *cis* configuration. These complexes of MoCl_4 were characterized by spectral and magnetic measurements.

Owing to the instability of the tetrahalides of molybdenum, few complexes with organic ligands have

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been formed by direct reaction. Previous to this study, complexes of MoBr_4 were unknown except for the hexabromo salts. It was desirable therefore to synthesize a series of octahedrally coordinated molybdenum(IV) bromide complexes for comparison with the reported MoCl_4 compounds so as to gain a better insight into the chemistry of molybdenum(IV) halides. Since molybdenum(IV) halides interact with many oxygen ligands by oxidation or solvolytic reaction, this study was restricted to a representative sampling of various nitrogen-containing ligands.

Experimental Section

General Precautions.—Since many of the compounds used in this study were unstable toward moisture and oxygen, all preparative and characterization operations were performed in a drybox under a dry argon atmosphere or on a vacuum line.

Materials.—Molybdenum metal was supplied by the Matheson-Coleman Co. Molybdenum pentachloride was obtained commercially from the Climax Molybdenum Co. and purified by sublimation before use. Reagent grade bromine was dried over phosphorus pentoxide for 48 hr, then thoroughly outgassed to *ca.* 10^{-5} mm. 2,2'-Dipyridyl was purified by repeated sublimation at *ca.* 10^{-5} mm. The ligands were dried with phosphorus pentoxide or barium oxide, thoroughly outgassed at *ca.* 10^{-5} mm, then vacuum distilled before use.

Analytical Methods.—Molybdenum was determined either by direct oxidation in a tared crucible or by α -benzoinoxime precipitation. In both cases, the molybdenum was weighed as molybdenum trioxide after ignition at 525° . Bromine and chlorine were determined as previously described.¹³ Nitrogen analysis was done by Midwest Microlab, Inc., Indianapolis, Ind. The apparent oxidation state of the metal in the complexes was determined by oxidation with excess potassium dichromate and back titration of the excess dichromate, as iodine from KI, with standard sodium thiosulfate.

X-Ray Diffraction Measurements.—All X-ray data were obtained using a Debye-Scherrer 114.59-mm diameter camera. Samples were passed through a 200-mesh sieve and packed in 0.3-mm glass capillaries. The samples were exposed to Ni-filtered $\text{Cu K}\alpha$ radiation for 4 hr on a General Electric XRD-5 with power settings of 50 kv and 16 ma. X-Ray diffraction data for the benzonitrile and 2,2'-dipyridyl complexes of MoCl_4 and MoBr_4 are as follows (the *d* spacings (Å) and the terms used for relative intensities are v, very; s, strong; m, medium; w, weak). $\text{MoCl}_4(\text{C}_7\text{H}_5\text{N})_2$: 8.36 m, 7.21 m, 6.60 m, 6.00 vs, 5.12 s, 4.90 m, 4.39 w, 4.00 vw, 3.67 vw, 3.57 vw, 3.39 w, 3.07 m, 2.64 w, 2.54 w, 2.30 w; $\text{MoBr}_4(\text{C}_7\text{H}_5\text{N})_2$: 8.63 s, 7.55 m, 6.85 m, 6.24 m, 5.18 vs, 4.87 vw, 3.43 m, 3.18 m, 3.01 w, 2.73 w, 2.60 w, 2.38 w, 2.26 vw, 2.07 vw; $\text{MoCl}_4(\text{C}_{10}\text{H}_8\text{N}_2)$: 7.69 m, 6.66 vw, 5.98 vs, 5.19 m, 4.53 vw, 4.29 m, 4.02 vw, 3.83 vw, 3.68 w, 3.47 m, 2.96 m, 2.59 w, 2.45 vw, 2.37 vw, 2.26 vw, 2.16 vw, 2.01 vw, 1.92 vw, 1.73 vw; $\text{MoBr}_4(\text{C}_{10}\text{H}_8\text{N}_2)$: 7.76 m, 6.81 s, 6.11 vs, 5.87 m, 5.34 m, 4.62 vw, 4.40 m, 4.13 m, 3.82 w, 3.56 s, 3.30 vw, 3.20 vw, 3.09 m, 2.98 vw, 2.88 vw, 2.63 m, 2.21 vw, 2.15 vw, 2.02 w, 1.83 vw.

Spectral Measurements.—Infrared absorption spectra were obtained with a Perkin-Elmer Infracord Model 137 using the KBr pellet technique. Repeated scans indicated the samples were stable for at least 0.5 hr.

Diffuse reflectance measurements were obtained on a Cary Model 14 spectrophotometer equipped with a diffuse reflectance attachment (Type I illumination) and a detector which allowed the region from 220 to 700 μ to be scanned. Samples were diluted with MgCO_3 in a drybox and firmly packed in a layer 1–2 mm thick against one face of a standard 1-cm square absorption cell. The sample was backed by a glass slide held firmly in place by a paper spacer and the cell sealed with a strip of tape.

Solution spectra were also obtained with the Cary Model 14. A cell similar to that described by McCarty and Torp¹⁴ was used. After each spectral measurement, the cell was opened and the solution removed for analysis.

Conductivity Measurements.—A conductivity cell with removable electrodes was constructed which allowed a weighed sample to be placed in the cell under an inert atmosphere. The apparatus was then evacuated on the vacuum line and the solvent distilled in from a weighing flask. An Industrial Instruments, Inc., conductivity bridge, Model RC-16B2, equipped with a maximum variable external capacitance of up to 0.1 μf was used for measurements.

Preparation of Halides.—Molybdenum tetrachloride was prepared by reduction of molybdenum pentachloride with benzene.¹⁵

Molybdenum tribromide was produced by the action of bromine on the metal at elevated temperature. This material was used to prepare molybdenum tetrabromide according to the method of Carnell and McCarty.¹⁶

Potassium hexachloromolybdate(IV) and rubidium hexabromomolybdate(IV) were prepared in a manner similar to that reported by Edwards, *et al.*⁹

Reactions.—Reactions at room temperature were carried out in vessels fitted with a Teflon-covered stirring bar, stopcock, and joint for attachment to the vacuum line. A finely ground sample, typically 2–5 g, was placed in the tared vessel in a drybox, evacuated, and weighed. Excess ligand (approximately 20 ml) was vacuum distilled into the vessel and the reaction allowed to proceed with stirring. At the end of a given time period, the excess ligand was distilled off and the residue vacuum dried at *ca.* 2×10^{-6} mm. Drying was continued until a constant weight was attained. In the case of 2,2'-dipyridyl, the tetrahalide was maintained at 100° with a large excess of 2,2'-dipyridyl in a sealed tube or at room temperature using benzene as a solvent. The excess 2,2'-dipyridyl was extracted with benzene. In the reactions where K_2MoCl_6 or Rb_2MoBr_6 were employed as starting materials, the resulting KCl or RbBr was separated from the molybdenum complex by extraction with acetonitrile. Table I summarizes the analytical results and some of the properties of the resulting compounds.

Results and Discussion

The direct reaction between the molybdenum tetrahalides and various nitrogen ligands proceeded slowly at room temperature. This is most likely due to the high lattice energies of the polymeric tetrahalides and consequently the rather low solubility of the halide in the reaction medium.

Molybdenum tetrachloride reacted directly with all of the ligands studied (N,N,N',N' -tetramethylethylenediamine, acetonitrile, propionitrile, benzonitrile, pyridine, and 2,2'-dipyridyl) to yield compounds of the type $\text{MoCl}_4 \cdot 2\text{L}$ or $\text{MoCl}_4 \cdot \text{B}$ (L = monodentate ligand, B = bidentate ligand). Molybdenum tetrabromide formed similar compounds only with acetonitrile, benzonitrile, and 2,2'-dipyridyl. The propionitrile complex of MoBr_4 was very unstable and at a pressure of *ca.* 10^{-5} mm all of the ligand was lost to yield the original MoBr_4 .

N,N,N',N' -Tetramethylethylenediamine reacted with MoCl_4 to form the monoadduct, $\text{MoCl}_4(\text{C}_6\text{H}_{16}\text{N}_2)$. This complex was only slightly soluble in the more polar solvents and apparently underwent solvolytic reaction with water, acetone, and dimethylformamide. Exposure to the atmosphere for a short period of time

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TABLE I
 REACTIONS OF MOLYBDENUM TETRAHALIDES WITH NITROGEN LIGANDS

Halide	Ligand	Calcd for			Found			Oxidn state	Color
		MoX ₄ ·2L or MoX ₄ ·B	% M	% X	% N	% M	% X		
MoCl ₄	C ₆ H ₁₆ N ₂	27.1	40.0	7.9	27.1	40.9	8.2	...	Red-brown
MoCl ₄	C ₂ H ₅ CN	27.6	40.7	8.1	27.4	41.0	8.0	3.95	Yellow-brown
MoCl ₄	C ₆ H ₅ CN	21.1	31.1	6.1	19.8	31.1	6.2	4.02	Yellow
MoCl ₄	C ₁₀ H ₈ N ₂	24.4	36.0	7.1	24.2	36.1	7.3	4.00	Yellow-green
K ₂ MoCl ₆	C ₁₀ H ₈ N ₂	24.4	36.0	7.1	24.0	36.1	7.3	3.98	Red
MoBr ₄	C ₆ H ₁₆ N ₂	No definite compound formation after 1-month reaction period							
MoBr ₄	(C ₂ H ₅) ₃ N	No definite compound formation after 1-month reaction period							
MoBr ₄	CH ₃ CN	19.3	64.2	5.6	19.2	62.2	5.6	3.98	Dark brown
MoBr ₄	C ₆ H ₅ CN	15.2	51.4	4.5	15.0	50.5	4.4	4.04	Dark green
MoBr ₄	C ₆ H ₅ N	Reduction to +3 state							
MoBr ₄ ^a	C ₁₀ H ₈ N ₂	16.8	56.0	4.9	16.2	55.8	5.1	3.94	Red-brown
Rb ₂ MoBr ₆	C ₁₀ H ₈ N ₂	16.8	56.0	4.9	16.5	55.6	5.0	3.95	Red

^a Reaction run in benzene as solvent. In molten 2,2'-dipyridyl at 100°, reduction was observed.

indicated that the compound was unstable toward air oxidation and hydrolysis, the formation of HCl being quite noticeable. In contrast, MoBr₄ does not appear to yield a well-defined monoadduct with this ligand and, in addition, reduction of the tetrabromide by N,N,N',N'-tetramethylethylenediamine was observed at higher temperatures (55°, 1 month). Analysis of the product obtained by adding an excess of the diamine to MoBr₄ at room temperature indicated a compound having a stoichiometry of approximately MoBr₄·C₆H₁₆N₂. An X-ray diffraction pattern, however, showed only lines attributable to MoBr₄. In addition, the diffuse reflectance spectrum contained only one very broad band in the visible region. These results are similar to those reported for the reaction between triethylamine and the niobium halides¹⁷ and suggest the formation of an amorphous compound having no definite composition. That MoBr₄ and N,N,N',N'-tetramethylethylenediamine do not form the monoadduct may at least partially be ascribed to steric factors, considering the bulk of both the tertiary amine groups and bromine atoms. It should be noted, however, that NbBr₄ does react with N,N,N',N'-tetramethylethylenediamine to form the monoadduct, NbBr₄·C₆H₁₆N₂.¹⁷

Pyridine is known to react with MoCl₄ to form the compound MoCl₄(C₅H₅N)₂.¹⁵ With longer reaction periods, reduction to MoCl₃(C₅H₅N)₃ is observed.¹⁸ Molybdenum tetrabromide was also observed to undergo reduction to the molybdenum(III) species, MoBr₃(C₅H₅N)₃, which has been prepared from MoBr₃ and pyridine.¹⁸ It was not possible to obtain a molybdenum(IV) bromide-pyridine product completely free of reduced product. The same difficulty was encountered with 2,2'-dipyridyl at elevated temperatures, reduction occurring to yield a molybdenum(III) species. The reduced species appears to be of the type Mo₂Br₆(C₁₀H₈N₂)₃ as prepared by Carmichael, *et al.*,¹⁹ from MoBr₃ and 2,2'-dipyridyl and not the [Mo(C₁₀H₈N₂)₃]³⁺·3X⁻ species reported by Steele.⁵ These

results are in line with the expected trend that, in general, bromides undergo reduction more readily than chlorides.

Of concern in this study was the preparation of compounds using different starting materials and reaction conditions. The major emphasis in this respect was with the reactions of 2,2'-dipyridyl with the possibility of obtaining compounds having different stoichiometry. Molybdenum tetrachloride with excess 2,2'-dipyridyl in benzene at room temperature or in molten 2,2'-dipyridyl at 100° gave a yellowish green product. The resulting compound was identified as MoCl₄(C₁₀H₈N₂). Saturated solutions of this compound in acetonitrile appeared stable and when evaporated under vacuum gave a dark brown, highly crystalline product which exhibited an X-ray diffraction pattern identical with that of the yellow-green form of MoCl₄(C₁₀H₈N₂). The reaction of potassium hexachloromolybdate(IV) with 2,2'-dipyridyl at 100° resulted in the formation of highly crystalline, dark reddish brown product which corresponded to MoCl₄(C₁₀H₈N₂). The X-ray diffraction data (Experimental Section) as well as infrared, visible, and ultraviolet spectra were identical with those of the yellow-green MoCl₄(C₁₀H₈N₂).

The color difference between the apparently equivalent forms of MoCl₄(C₁₀H₈N₂) may possibly be accounted for on the basis of different size or crystal habit. This dissimilarity would be expected, considering the two modes of crystallization: (1) rapid precipitation, upon formation, from a solvent (benzene or molten 2,2'-dipyridyl) in which the complex shows relatively no solubility (the yellow-green form) and (2) slow crystallization from a saturated solution, yielding a highly crystalline product (the red-brown form).

Molybdenum tetrabromide was observed to undergo reduction with molten 2,2'-dipyridyl at 100°. The red-brown compound MoBr₄(C₁₀H₈N₂) was obtained, however, from the reaction between MoBr₄ and 2,2'-dipyridyl in benzene at room temperature and from the reaction of Rb₂MoBr₆ in molten 2,2'-dipyridyl at 90°. It is apparent that the hexabromo salt is a more desirable starting material at elevated temperatures since reduction is observed in the reaction between MoBr₄

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and 2,2'-dipyridyl. This is not unexpected as MoBr_4 is known to be unstable at these temperatures and some decomposition to MoBr_3 and Br_2 could occur.¹⁶ The fact that MoBr_4 involves reduction and Rb_2MoBr_6 does not lead to the possibility that reduction occurs *via* decomposition of MoBr_4 followed by complexation of the resulting MoBr_3 .

We have also observed the reduction of MoCl_5 to $\text{MoCl}_4(\text{C}_{10}\text{H}_8\text{N}_2)$ as reported by Carmichael, *et al.*¹⁹ These authors were unable, however, to obtain the pure compound. It appears that this is due to incomplete removal of 2,2'-dipyridyl and oxidation products as their analyses indicate 2,2'-dipyridyl to be in excess of that required for $\text{MoCl}_4(\text{C}_{10}\text{H}_8\text{N}_2)$. Furthermore, these authors report that the presence of the protonated 2,2'-dipyridyl, $[\text{dipyH}_2]^{2+}$, was not observed. Studies on the reduction of WCl_6 and WBr_5 with 2,2'-dipyridyl indicate the formation of the protonated species, $[\text{dipyH}]^+$.²⁰ In any event, we have found that it is possible to obtain a pure reduced species by heating the product at *ca.* 70° under a dynamic vacuum (*ca.* 10^{-5} mm) after extraction with benzene. This heating procedure removes the last traces of the protonated species. Additional work on the mechanism of these reductions as well as the reduction of MoBr_4 is being carried out and will be reported at a later date.

Infrared data for all well-defined products were obtained from 660 to 4000 cm^{-1} . This was done primarily for a qualitative indication of the presence of uncoordinated solvent, water, or other impurities. The resulting spectra indicated peaks typical of the coordinated ligands and gave no evidence for structures other than those in which the ligands are coordinated to molybdenum(IV) halide. Examination of the infrared spectrum of $\text{MoCl}_4(\text{C}_{10}\text{H}_8\text{N}_2)$ obtained by dissolving the yellow-green form in acetonitrile did not indicate the presence of nitrile in the complex, demonstrating that acetonitrile will displace neither 2,2'-dipyridyl nor halide in the complex.

The X-ray powder diffraction patterns of the chloride and bromide complexes of benzonitrile showed them to be isomorphous as are also the 2,2'-dipyridyl adducts. These compounds, however, were not sufficiently soluble in noncoordinating organic solvents for molecular weight data to be obtained. The conductivity of the molybdenum complexes was measured in *ca.* 10^{-3} M solutions, and, in all cases, the compounds were found to be essentially nonelectrolytes. Thus, while it is not possible to characterize unambiguously the resulting complexes as being monomeric, these results in addition to the spectra discussed below appear to indicate the presence of six-coordinate molybdenum species. The results reported by Fowles and co-workers on similar compounds also support this conclusion.¹²

The visible and ultraviolet spectra obtained for the various molybdenum(IV) complexes are summarized in Table II. The expected sixth peak in MoCl_4 -

TABLE II
SPECTRA OF MOLYBDENUM COMPLEXES IN
ACETONITRILE SOLUTION^a

Compound	Peak positions, ^b cm^{-1}
$\text{MoCl}_4(\text{C}_2\text{H}_5\text{CN})_2$	20,000 (50), 25,000 (1500), 27,800 (1750), 32,200 (4500), 34,600, 41,000
$\text{MoCl}_4(\text{C}_6\text{H}_5\text{N}_2)$	19,000 (250), 22,700 (300), 32,200 (2500)
$\text{MoCl}_4(\text{C}_6\text{H}_5\text{CN})_2$	19,600 (140), 23,000 (1200), 27,400 (2900), 30,500 (10,500), 34,800 (39,000), 35,700 (40,000), 36,600 (33,000)
$\text{MoCl}_4(\text{C}_{10}\text{H}_8\text{N}_2)$	19,300 (100), 25,000 (1200), 27,400 (2400), 33,300 (13,000), 41,700 (14,000), 46,500 (13,000)
$\text{MoBr}_4(\text{CH}_3\text{CN})_2$	16,260 (190), 21,050 (1050), 24,210 (2150), 26,320 (3250), 31,450 (6250)
$\text{MoBr}_4(\text{C}_6\text{H}_5\text{CN})_2$	16,400 (270), 20,960 (1040), 23,870 (2380), 26,450 (3600), 36,300, 37,000
$\text{MoBr}_4(\text{C}_{10}\text{H}_8\text{N}_2)$	18,000 (170), 21,300 (800), 24,200 (2300), 25,800 (2250), 33,300 (33,000), 41,700 (24,000), 46,500 (33,000)

^a Peak positions without extinction coefficients were obtained from diffuse reflectance spectra. ^b Molar extinction coefficients in parentheses.

$(\text{C}_2\text{H}_5\text{CN})_2$ which was not found by Allen, *et al.*,¹¹ was observed as a shoulder at 27,800 cm^{-1} . Inspection of Table II shows the complexity of the spectra of these compounds. The intricacy of the spectra renders it difficult to assign unambiguously specific transitions to the observed bands. Assignment of the lowest energy band to the one-electron ${}^3\text{T}_1 \rightarrow {}^3\text{T}_2$ transition may be reasonable. The observed molar extinction coefficients are compatible with those expected for a d-d transition ($\epsilon \sim 200$). The second bands ($\sim 25,000$ and $\sim 21,000$ cm^{-1} for the chloride and bromide complexes, respectively) exhibit rather high molar extinction coefficients for the ${}^3\text{T}_1 \rightarrow {}^3\text{T}_1(\text{P})$ transition, as assigned by Fowles.¹² The higher intensity of this band in the complexes may reflect the presence of a considerable amount of vibronic coupling and/or vibronically induced borrowing of intensity from the strong ultraviolet absorption bands. The third bands ($\sim 27,000$ and $\sim 24,000$ cm^{-1} for the chloride and bromide complexes, respectively) have extinction coefficients much higher than those expected for a third d-d ligand field transition, although one might expect it to occur in this region of the spectrum. The energy of these bands is rather low for a ligand-to-metal charge transfer; however, a transition of this type could account for these bands and cannot be ruled out at this time.

The transitions exhibited by the 2,2'-dipyridyl complexes at 33,300 and 41,700 cm^{-1} may be ascribed to charge transfer within 2,2'-dipyridyl. Leontev, *et al.*, described these transitions in pure 2,2'-dipyridyl and attributed them to bonding-antibonding transitions ($\pi-\pi^*$).²¹ Similarly, the observed transitions at 34,800, 35,700, and 36,600 cm^{-1} in the benzonitrile complexes are most likely due to transitions within the ligand. This does not, however, preclude the possible

(20) T. M. Brown and S. DeLong unpublished observations.

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presence of some ligand-metal charge-transfer bands which may be obscured by the higher intensity intraligand transitions. Corresponding bands in the other

complexes were less well-defined and of lower intensity. These may be due to similar intraligand or ligand-metal electron transfer.

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Porphyryns. V. Extended Hückel Calculations on Vanadyl (VO²⁺) and Vanadium(II) Complexes

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The extended Hückel model is applied to VO²⁺ and V²⁺ porphyrins. VO is predicted to be out of plane; energies for d → d transitions are given. V is calculated to be stable, but subject to ready oxidation by O₂.

Introduction

Vanadyl porphyrins, in which VO replaces the H₂ of the free base, are widely distributed in nature in a variety of natural bitumens¹ and have become of theoretical interest, especially since epr studies have begun to shed light on the electronic structure of the vanadium orbitals.²⁻⁶ There are, in addition, several other interesting phenomena which a quantum mechanical study of vanadium porphyrins might attempt to explain. Foremost among these is the apparent chemical instability of vanadium(II) porphyrins, *i.e.*, compounds where V alone replaces H₂ in the free base. We report in this work the results of a study of vanadyl and vanadium porphyrins using the extended Hückel model.⁷⁻¹⁰ A previous investigation of vanadyl compounds by Ballhausen and Gray¹¹ has already gone a good way in explaining the quantum mechanical nature of VO in complexes in which V is penta- or hexacoordinated. Included in their calculations are the 3d, 4s, 4p orbitals of V, the valence orbitals of oxygen, and the sp³ hybrids and p_π orbitals of the chelating atoms of the ligand groups. Their calculation is of the extended Hückel type, with provision made for atomic charge consistency. Our calculations are similar, but include all the valence orbitals of all the atoms in the porphyrin system.

Method

We seek solutions to the eigenvalue equation

$$H_{\text{eff}}\phi_j = w_j\phi_j$$

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where H_{eff} is an effective one-electron Hamiltonian for the molecule. The molecular orbitals (MO) ϕ_j are expanded on a minimal basis set of atomic orbitals (AO), χ_p

$$\phi_j = \sum_p \chi_p c_{pj}$$

This leads to a secular equation

$$\det|H_{pq} - wS_{pq}| = 0$$

in which

$$S_{pq} = \int dv \chi_p \chi_q$$

$$H_{pq} = \int dv \chi_p H_{\text{eff}} \chi_q$$

In the extended Hückel model the latter are approximated by

$$H_{pq} = 1/2 S_{pq} (H_{pp} + H_{qq}) [\kappa - (\kappa - 1) \delta_{pq}]$$

In the above κ is a pure parameter and H_{pp} are determined from atomic ionization processes. The methods of determining H_{pp} are described in more detail elsewhere and values for H, C, and N have been given in calculations reported on other metal porphyrin systems.⁹ The values for V and O are given in Table I and were obtained by the same methods.^{9, 10, 12, 13}

Since ionization processes are highly dependent on net atomic charge, a self-consistent charge procedure was employed as in previous work.⁹ A first calculation using H_{pp} for neutral atoms is carried out. Then H_{pp} are readjusted to be more in accord with the net charge on atom p calculated by a Mulliken population analysis.¹⁴ A second calculation follows. Iterations continue until the calculated and assumed atomic charges agree to within 0.05 electron. This procedure greatly moderates charge buildup.

The AO basis set we use is

$$\chi(n, l, m) = N r^{n-1} \exp(-\zeta r) Y_l^m(\theta, \Phi)$$

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