magnetic. In an ion of the symmetry corresponding to these *trans* complexes, the presence or absence of paramagnetism is dependent on whether the d_{xy} orbital is lower or higher than the degenerate d_{xz} and d_{yz} orbitals. The present results are consistent with the view that the d_{xy} orbital is lowest, as suggested by Lippard.[12]

Acid Ionization Constants.—Litvinchuk and Mikhalevich[30] reported measurements of hydrolysis constants at 16° for reactions of the type

$$Mo(OH)_4(CN)_4{}^{4-} + H_2O \rightleftharpoons Mo(OH)_3(H_2O)(CN)_4{}^{3-} + OH^-$$

Although we would formulate this reaction as

$$MoO_2(CN)_4{}^{4-} + H_2O \rightleftharpoons MoO(OH)(CN)_4{}^{3-} + OH^-$$

the numerical value of the constant is the same regardless of the formulation. Their values result from measurements of the pH of solutions of the appropriate salts. Although this method is satisfactory in principle, its success is dependent on using a salt quite free of the conjugate acid or conjugate base of the anion whose hydrolysis is being measured. Our experience indicates that this would be easy with $K_4[MoO_2(CN)_4$, difficult with $K_3[MoO(OH)(CN)_4]$, and very difficult with $K_2[Mo(OH)_2(CN)_4]$. The pH's they report for solutions of $K_2[Mo(OH)_2(H_2O)_2(CN)_4]$ are more basic than those we observe with $K_2[Mo(OH)_2(CN)_4]$, although these must be a single compound. Their value for the acid ionization constant of $MoO(OH)(CN)_4{}^{3-}$, calculated from the hydrolysis of $MoO_2(CN)_4{}^{4-}$, is meaningful, but the other two constants are probably not. Their value is 2.2×10^{-13} at 16°.

We have used data, like those in Figure 1, from the titration of $MoO_2(CN)_4{}^{4-}$ to calculate the acid ionization constants. In these calculations a value of 0.8 was used for the activity coefficients of H^+ and OH^-. The following values were obtained for acidionization constants at 25°: for $MoO(OH)(CN_4{}^{3-}$, $K_a = 2.4 \times 10^{-13}$; for $Mo(OH)_2(CN)_4{}^{2-}$, $K_a = 1.05 \times 10^{-10}$.

Visible and Ultraviolet Spectra.—Use of the ionization constants allows an estimate of the relative amounts of the various ions in a solution of fixed pH. Such values are indicated by the symbols F_{II}, F_{III}, and F_{IV} (the subscript indicates the charge of the complex) in Tables I and II for comparison with the visible and uv spectral data. The values are included to indicate in a general way the relative abundance of the three complexes; the exact numerical values cannot be correct because of changing activity coefficients in the diverse media used.

It appears that each of the three complexes has a charge-transfer absorption with a peak at 226 mμ. Solutions of acidic pH have a characteristic absorption peak at 299 mμ, but the species has not been identified.

In the visible region the absorption spectra at different pH's are similar enough so that all solutions have a color with a blue component. It appears that λ_{max} values for the individual species are approximately as follows: $MoO_2(CN)_4{}^{4-}$, somewhat less than 594 mμ; $MoO(OH)(CN)_4{}^{3-}$, about 595 mμ; $Mo(OH)_2(CN)_4{}^{2-}$, about 620 mμ; species present at pH <7, about 610 mμ. Apparently these absorption maxima can be shifted in the solid state, probably as a result of the varying proximity and influence of cations. For example, a KBr pellet of the red-violet compound showed a maximum at 520 mμ. The proximity of cations also affects the color *via* the effect on the high-intensity charge-transfer bands whose tails may come into the visible region. This effect is more apparent in the solids containing $Mo(OH)_2(CN)_4{}^{2-}$. The solid with the cation $Cd(H_2O)_6{}^{2+}$ is blue-purple, that with the cation K^+ is green, and that with the cation Cd^{2+} is brown-green.

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α-Molybdenum Tetrachloride. A Structural Isomer Containing Molybdenum–Molybdenum Interactions

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Received April 29, 1968

Molybdenum pentachloride reacts with tetrachloroethylene in carbon tetrachloride solution to give a new form of molybdenum tetrachloride which is isomorphous with the metal–metal bonded niobium tetrachloride. The magnetic properties however indicate that the molybdenum–molybdenum double bond is not completely formed, and this behavior is discussed.

Introduction

A previously reported form of molybdenum tetrachloride shows normal paramagnetic behavior for two unpaired electrons.[1] The structure consists of isolated $MoCl_6$ octahedra together with octahedra sharing edges, and the shortest molybdenum–molybdenum distance of 3.50 Å precludes the presence of significant molybdenum–molybdenum interactions.[1] This is in contrast to the tetrachlorides of the neighboring elements in the periodic table. For example the for-

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[1] H. Schafer, H. G. Schnering, J. Tillack, F. Kuhnen, H. Wohrle, and H. Bauman, *Z. Anorg. Allgem. Chem.*, **353**, 281 (1967).

mally d^1 niobium and tantalum tetrachlorides and the formally d^2 tungsten tetrachloride are diamagnetic and isomorphous[2] and consist of infinite strings of octahedra sharing opposite edges, the metal–metal distances being alternately short and long confirming the existence of direct metal–metal bonding.[3] Strong metal–metal bonding also occurs in rhenium tetrachloride, although in this case the bonding is through a common octahedral face between two metal atoms.[4] Technetium tetrachloride, on the other hand, shows normal paramagnetic behavior,[5] and its structure confirms the absence of direct technetium–technetium bonding.[6]

Experimental Section

Magnetic Measurements.—Susceptibilities were measured by the Faraday method using a Teflon bucket and lid, with an air-tight neoprene O-ring seal. Silver was used as calibrant,[7] and standard diamagnetic corrections were applied.[8]

X-Ray Measurements.—A Hägg 8-cm Guinier focusing camera using Ni-filtered Cu Kα radiation was used. Samples were mounted in flattened glass capillaries. Thorium dioxide was included in the samples as an internal calibrant. Intensities were estimated visually.

Materials.—Molybdenum pentachloride (K & K Laboratories) was purified by vacuum sublimation. *Anal.* Calcd for $MoCl_5$: Cl, 64.9; Found: Cl, 63.6. Niobium tetrachloride was prepared as described previously.[9] Solvents were dried and purified as before.[10] Tetrachloroethylene was purified[11] and distilled from phosphorus pentoxide before use.

Molybdenum Tetrachloride.—All operations were conducted under dry, oxygen-free conditions on a standard vacuum system.[10] In a typical preparation, molybdenum pentachloride (4.0 g) was washed free from oxychlorides with dry carbon tetrachloride and then refluxed under slightly reduced pressure for 2.5 days in a mixture of carbon tetrachloride (50 ml) and tetrachloroethylene (20 ml). The crystalline residue was filtered, washed with carbon tetrachloride, and dried for several hours under vacuum. If the reaction was stopped before 2 days, excess molybdenum pentachloride had to be sublimed from the solid. The black product is completely soluble in dilute hydrochloric acid showing the absence of lower chlorides. *Anal.* Calcd for $MoCl_4$: Mo, 40.4; Cl, 59.6. Found: Mo, 40.1; Cl, 59.4. The X-ray data are given as *d*(obsd), *I* values: 9.092, 5; 6.099, 100; 5.888, 100; 5.383, 5; 5.274, 5; 5.091, 10; 4.866, 10; 4.618, 10; 4.444, 80; 4.386, 5; 4.042, 80; 3.266, 30; 2.936, 5; 2.856, 30; 2.750, 5; 2.705, 5; 2.632, 100; 2.602, 25; 2.522, 25; 2.491, 2; 2.365, 2; 2.320, 2; 2.270, 2; 2.221, 50; 2.184, 20; 2.131, 20; 2.102, 50; 2.075, 1; 2.012, 50; 1.961, 2; 1.897, 5; 1.863, 5; 1.838, 30; 1.811, 2; 1.753, 2; 1.721, 40; 1.679, 1; 1.633, 30; 1.586, 30; 1.572, 2; 1.506, 10; 1.467, 10; 1.457, 2; 1.385, 5; 1.374, 5; 1.348, 2; 1.336, 2.

Results and Discussion

The reaction of molybdenum pentachloride in refluxing tetrachloroethylene and carbon tetrachloride yields molybdenum tetrachloride as a pure, crystalline compound. It is convenient to label this isomer α-$MoCl_4$ because of its similarity with other tetrachlorides, and the unique structural isomer obtained at high temperatures described by Schafer, *et al.*,[1] and also by Couch and Brenner,[12] as the β isomer. It is probable that this α isomer has been obtained previously but never in a sufficiently pure state to allow characterization. The reduction of molybdenum pentachloride with refluxing benzene yielded a tetrachloride contaminated with carbonaceous material with a magnetic moment at 25° of 0.93 BM,[13] similar to that obtained in this work. The product from the reaction of molybdenum pentachloride with cetane or paraffin was possibly similar, but again contaminated with carbonaceous material.[14]

The X-ray powder pattern of α-molybdenum tetrachloride is very similar to that of niobium tetrachloride, indicating that the two compounds are isomorphous. On this basis, approximate cell dimensions are $a = 12.3$, $b = 6.4$, $c = 8.4$ Å, and $\beta = 134°$.

The room-temperature effective magnetic moment of α-molybdenum tetrachloride is 0.85 BM, and it is found to follow the Curie–Weiss law with $\theta = 220°$ (Table I). The susceptibility is independent of field strength. α-Molybdenum tetrachloride is therefore not completely diamagnetic as might be expected from its structure, nor does it approach the room-temperature effective magnetic moment of 2.42 BM found for the nonmetal–metal bonded β-molybdenum tetrachloride,[1] but is intermediate between these two extremes. The magnetic susceptibility arising from magnetic exchange between pairs of metal atoms has been given[15] as a function of the *g* factor, the exchange integral, and the contribution from temperature-independent paramagnetism. We find that it is not possible to fit the experimental data using any combination of these variables, irrespective of whether it is considered that both electrons on each metal atom couple equally or whether one is being completely used for metal–metal bonding and the other exchanging more weakly. In all cases the calculated magnetic moment

TABLE I

MAGNETIC DATA FOR α-$MoCl_4$

Temp, °K	$10^6\chi_g$, cgsu	μ_{eff}, BM	Temp, °K	$10^6\chi_g$, cgsu	μ_{eff}, BM
309.3	0.831	0.85	194.4	1.125	0.75
299.6	0.856	0.85	180.8	1.224	0.75
285.7	0.873	0.83	165.1	1.272	0.73
269.4	0.897	0.82	113.2	1.712	0.67
253.8	0.946	0.81	98.6	1.916	0.66
238.7	0.970	0.79	89.0	2.105	0.65
223.0	1.036	0.78	86.3	2.145	0.65
209.0	1.101	0.77			

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falls much more steeply with decreasing temperature than is experimentally observed. We conclude that there is additional weaker magnetic exchange between different pairs of molybdenum atoms, such that it is continuous parallel to the *b* axis.

Such intermediate magnetic behavior for a metal–metal bonded halide is very unusual, but not unique, as it has also been observed in salts of $Mo_2Cl_9^{3-}$,[16] and also for a number of halides of unknown structure.[17]

Metal–metal bonding normally requires expanded d orbitals arising from a low effective nuclear charge on the metal atom, which for a ligand such as chloride can be achieved as follows:[18] (a) An early transition metal is required as is illustrated by the metal–metal bonding found in $TiCl_3$, but not in VCl_3 or $CrCl_3$; in $HfCl_3$, $TaCl_3$, WCl_3, and $ReCl_3$, but not in $OsCl_3$ or $IrCl_3$; and in $NbCl_4$ with α-$MoCl_4$ marginal, but not in β-$MoCl_4$ or $TcCl_4$. (b) A heavy transition metal is favorable as is illustrated by the metal–metal bonding in $TaCl_3$ and $NbCl_3$, but not in VCl_3; in $TaCl_4$ and $NbCl_4$, but not in VCl_4; in $ReCl_4$ but not in $TcCl_4$; and in WCl_4 with α-$MoCl_4$ marginal, but not in β-$MoCl_4$. (c) Similarly a relatively low formal oxidation state is required as is illustrated by the metal–metal bonding in WCl_2, WCl_3, and WCl_4, but not in WCl_5; and in $MoCl_2$ and $MoCl_3$ with α-$MoCl_4$ marginal, but not in β-$MoCl_4$ or $MoCl_5$. It can be seen that the behavior of α-$MoCl_4$ is consistent with this general pattern.

Acknowledgments.—We are grateful for the award of a University Research Studentship to R. M.

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A Molecular Orbital Study of Vibronic Interactions in the $CuCl_2$ Molecule

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Received May 16, 1968

Semiempirical LCAO–MO calculations of the extended Hückel type are described for the triatomic molecule $CuCl_2$. Potential curves for both ground and excited states are presented, and computed vibrational frequencies are compared with experimental values. Spin–orbit coupling is found to alter significantly the bending curves for the Renner-active $^2\Pi_g$ and $^2\Delta_g$ crystal-field states, reducing the tendency of the linear molecule to bend on excitation. Electric-dipole oscillator strengths are computed for both the Laporte-allowed charge-transfer and the vibronic crystal-field electronic transitions. All intensities are greatest when the electric vector is parallel to the bond axis. The bending mode appears to be more effective than the antisymmetric stretching mole in inducing intensity, partly because the lower frequency of the former implies a larger temperature factor in comparing the results to the measurements of DeKock and Gruen made at 1076°K. Distribution of the vibronic intensity over spin–orbit levels is found to bring in contributions proportional to differences of the *diagonal* dipole moments of the various crystal-field states of a C_{∞} or C_{2v} deformed molecule. The energy level and intensity calculations tend to confirm the spectral assignments of DeKock and Gruen, as opposed to those of Hougen, Leroi, and James, although some difficulty remains in obtaining sufficient vibronic intensity for the $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ absorption band, unless this band overlaps the lower energy and stronger $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ band.

Introduction

The extended Hückel type of semiempirical LCAO–MO (linear combination of atomic orbitals–molecular orbital) scheme[2] has proved useful in describing vibronic interactions in various transition metal complexes, including the tetrahedral species[3] VCl_4 and $CuCl_4^{2-}$ and the octahedral complex[4] $CuCl_6^{4-}$. For these interesting Jahn–Teller systems the method yielded not only potential surfaces that were semiquantitatively correct but also wave functions from which oscillator strengths were calculated for the various crystal-field (d–d) electronic transitions. As a continuation of these studies, we present here the results of applying the MO method to the triatomic molecule $CuCl_2$. Of particular interest are the effect of bending on the orbitally degenerate $^2\Pi_g$ and $^2\Delta_g$ excited electronic states and the influence of spin–orbit coupling in modifying this Renner[5] behavior. Considerable infrared[6] and electronic[7,8] spectral data are available from gas-phase measurements for this and other[9] transition metal dihalides, while an electron spin resonance (esr) study[10] has been

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