Notes

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An Improved Method for the Preparation of Tungsten Pentachloride and Molybdenum Tetrachloride[1]

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In addition to the known thermally induced dissociation of tungsten hexachloride[2,3] and molybdenum pentachloride,[2] there is evidence that these species undergo partial reduction in nonaqueous solvents even in the absence of ligands.[4-6] The complete reduction of molybdenum pentachloride to molybdenum tetrachloride with benzene has also been reported.[7] Recent work in our laboratories indicated that the reduction of tungsten hexachloride in the presence of certain ligands such as 2,2′-bipyridine, 3-chloropyridine, and acetonitrile most likely proceeds *via* dissociation of chlorine. The function of the ligand is to stabilize the metal in a lower oxidation state and possibly to remove chlorine from solution. These results led us to consider a new method for the preparation of lower halides, in particular, tungsten pentachloride.

Results and Discussion

Preparation of Tungsten Pentachloride and Molybdenum Tetrachloride.—It is well known that chlorine will add photolytically to the double bond of tetrachloroethylene to produce hexachloroethane.[8] By removing chlorine in this manner from solutions of tungsten hexachloride and molybdenum pentachloride in tetrachloroethylene, high yields of tungsten pentachloride (>90%) and molybdenum tetrachloride (85–95%) were obtained.

The completeness of reaction, the ease of isolation of the product, and the high purity of the tungsten pentachloride obtained from tetrachloroethylene solutions provides a quicker and cleaner method of preparation than those used previously[9-14] and can be more readily scaled up to produce larger quantities of this material. Although the phosphorus reduction of tungsten hexachloride to yield tungsten pentachloride may appear to be comparable, the use of tetrachloroethylene avoids possible phosphorus contamination and requires less manipulation. Tungsten tetrachloride is also formed in small amounts by our method, but the long reaction time required for complete conversion makes it unsuitable as a means for its preparation at the present time, *i.e.*, only a 50% yield is obtained even after 3 days reaction at 150°.

The preparation of molybdenum tetrachloride in this fashion suffers from being time consuming, but, as in the method of Larson and Moore,[7] sublimation purification is unnecessary and the known facile disproportionation of the product is circumvented. An advantage over the method of Larson and Moore is the absence of undesirable carbonaceous materials which often result in the benzene reduction. As with the benzene reduction, it is important that the pentachloride used in the reaction with tetrachloroethylene be free from impurities, particularly oxychlorides.

Niobium and Tantalum Pentachlorides and Tungsten Oxytetrachloride.—Extension of the method involving the use of tetrachloroethylene to niobium and tantalum pentachlorides met with little success. Only a 14% yield of niobium tetrachloride was obtained, and tantalum pentachloride did not react at all after 2 weeks. An 18% yield of tungsten oxytrichloride was obtained from the oxytetrachloride. Additional work is necessary to find the optimum conditions for the formation of these compounds.

Structure of Molybdenum Tetrachloride.—Of considerable interest is the structure of the $MoCl_4$ obtained from the reduction of $MoCl_5$ in tetrachloroethylene. The X-ray powder diffraction data of the tetrachloride agree with the results obtained by Larson and Moore[15] but differ from the data reported by other workers.[16,17] In this respect it appears that the $MoCl_4$ obtained by our method and that from $MoCl_5$ in liquid benzene are similar in structure. A closer examination of the X-ray data revealed a striking resemblance to the patterns of the niobium[18] and tungsten[13] tetrachlorides. Schnering and Wöhrle[19] found from single-crystal data that $NbCl_4$ is monoclinic with $a = 12.32$, $b = 6.82$, $c = 8.21$ Å, and $\beta = 134°$. The X-ray data of the $MoCl_4$ reported here can also be indexed on a monoclinic unit cell but of dimensions $a = 12.33$, $b = 6.78$, $c = 8.22$ Å, and $\beta = 134°$. In addition, the far-infrared spectrum of this $MoCl_4$ is very similar to that

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(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

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of WCl_4 (major absorptions occurred at 404, 350, and 268 cm^{-1} for $MoCl_4$ and at 392, 358, and 243 cm^{-1} for WCl_4). Thus it appears that this method of preparation is somewhat unique in that it yields a compound which is isomorphous with the corresponding tetrahalides of niobium and tungsten. However, unlike $NbCl_4$ and WCl_4 which have been found to be diamagnetic, this $MoCl_4$ exhibits very weak paramagnetism. The uncorrected molar susceptibility of the tetrachloride from two different preparations was found to be $+80$ and $+101 \times 10^{-6}$ cgs unit/mol at 24°. These values correspond to effective magnetic moments of 0.67 and 0.71 BM, respectively, which are somewhat lower than the values of 0.934 BM reported by Larson and Moore.[7] Considering the possible structure of $MoCl_4$, this low moment is most likely due to extensive coupling of the $4d^2$ electrons between adjacent molybdenum atoms.

By heating our $MoCl_4$ to 250° in the presence of $MoCl_5$ vapors, the structure changes to the form reported by Schafer, *et al.*,[17] and Couch and Brenner.[16] After this conversion, good agreement with the above reports is obtained for the X-ray powder diffraction and magnetic data, and the far-infrared spectrum further substantiates that a different form of $MoCl_4$ results at the high temperature. The tetrachloride obtained in this fashion appears to be more thermally stable than that obtained from the low-temperature reactions.

Experimental Section

Since the chlorides of tungsten and molybdenum are unstable in air, all operations were carried out using standard vacuum line and drybox techniques. The WCl_6 and $MoCl_5$ (both from Climax Molybdenum Co.) were fractionally sublimed *in vacuo* before use. The tetrachloroethylene (Eastman Organic Chemicals) was treated with Drierite, degassed to *ca.* 10^{-5} mm, and vacuum distilled onto previously degassed Linde Type 4A Molecular Sieves. The metal halides were analyzed using methods previously described.[13,20] X-Ray powder diffraction data were obtained using a Debye–Scherrer 114.59-mm powder camera. The samples were powdered, passed through a 200 mesh sieve, and packed in a 0.3-mm glass capillary under a nitrogen atmosphere. The samples were then exposed to nickel-filtered Cu Kα radiation for 7.5 hr on a General Electric XRD-5 with power settings of 50 kV and 16 mA. Magnetic susceptibility measurements were made between liquid-nitrogen and room temperatures using the Faraday technique. The data were corrected for the diamagnetism of the Teflon container and the diamagnetic contributions of the atom cores.[21,22] Far-infrared data were taken on a Beckman IR-12 grating spectrophotometer using Nujol mulls between $^1/_{32}$-in. polyethylene plates.

Reduction of Tungsten Hexachloride in Tetrachloroethylene.—WCl_6 (4.7 g) was stirred with 25 ml of tetrachloroethylene in an oil bath at 100° in the presence of strong light. After 24 hr, the organic material was removed by distillation *in vacuo* and the resulting product sublimed at 180°. These steps were carried out in an all glass, grease-free reaction tube. The dark blue-green crystalline sublimate melted at 246° (lit.[12] mp for WCl_5 248°) and its vapor had a color characteristic of WCl_5. Its X-ray powder diffraction pattern was identical with that of an analyzed sample of WCl_5 prepared from the disproportionation of WCl_4. Yields based on the weight of WCl_6 used were 90–94%. *Anal.* Calcd for WCl_5: W, 50.91; Cl, 49.09. Found: W, 50.93; Cl, 49.05; Cl:W atom ratio, 5.00.

A small amount of brown material remained behind after the sublimation process, but upon heating it to 350° more WCl_5 was produced along with a light tan solid; this is characteristic of the disproportionation of WCl_4.[13] The X-ray powder diffraction pattern of this product was identical with that of a sample previously identified as WCl_4.

Gas chromatographic analysis of the organic material showed the presence of excess starting material and C_2Cl_6 (92–98% of theory). The C_2Cl_6 isolated from this mixture melted at 186° (lit.[8] mp 187°) and had an infrared spectrum identical with that of a known sample.

The same reaction was run in the dark at 100° and the blue crystals obtained melted at 278° (lit.[12] mp for WCl_6 275°). Gas chromatographic analysis of the organic portion showed the presence of starting material only. Similarly, the reaction of WCl_6 with tetrachloroethylene at room temperature resulted in the formation of only small amounts (<10%) of WCl_5.

Reduction of Molybdenum Pentachloride in Tetrachloroethylene.—$MoCl_5$ (4.7 g) was stirred in 50 ml of tetrachloroethylene for 4 days at 100° in an oil bath. The vessel used allowed for filtration and extraction of the product, as was previously described.[20] After the allotted reaction time, the mixture was filtered and continuously extracted for 12 hr. This removed any C_2Cl_6 and excess $MoCl_5$. The $MoCl_4$ was then dried on the vacuum line producing a black powder in yields of 85–95% based on the weight of the starting $MoCl_5$. By gas chromatography 88% of the theoretical amount of C_2Cl_6 was detected in a typical analysis of the organic portion. Treatment of the $MoCl_4$ prepared in the above fashion with 6 *N* HCl revealed that only 0.09% was insoluble and infrared data indicated the presence of small amounts of organic impurity. *Anal.* Calcd for $MoCl_4$: Mo, 40.35; Cl, 59.65. Found: Mo, 39.84; Cl, 59.35; Cl:Mo atom ratio, 4.03.

In another preparation, it was found that, by starting with extremely pure $MoCl_5$ and extracting only until the extract was clear and colorless (4 hr), a purer product of $MoCl_4$ could be obtained; *i.e.*, a negligible amount of insoluble material was obtained by treatment with 6 *N* HCl and no organic impurities were detected by infrared analysis. *Anal.* Found: Mo, 40.34; Cl, 59.86; Cl:Mo atom ratio, 4.02.

The chemical properties of $MoCl_4$ prepared from solutions of tetrachloroethylene were similar to those reported by Larson and Moore.[7] The X-ray powder diffraction data for $MoCl_4$ produced by this method are as follows (the *d* spacings are in Å and the relative intensities are given in parentheses, 10 being highest): 6.01 (10), 4.44 (8), 4.02 (7), 3.27 (5), 2.96 (1), 2.83 (4), 2.74 (1), 2.64 (9), 2.59 (4), 2.54 (3), 2.22 (4), 2.17 (1), 2.13 (1), 2.10 (4), 2.01 (5), 1.91 (1), 1.83 (1), 1.72 (5), 1.68 (2), 1.64 (2), 1.61 (2), 1.58 (4), 1.50 (1), 1.47 (1), 1.38 (1), 1.34 (1), 1.31 (1), 1.29 (1), 1.27 (1).

A portion of the $MoCl_4$ formed from the tetrachloroethylene reduction of $MoCl_5$ was heated in a sealed tube to 250° in the presence of $MoCl_5$ vapors for 24 hr. During this process the $MoCl_4$ powder became very crystalline in appearance. The $MoCl_5$ was then removed by sublimation at 125°. The X-ray powder diffraction data for this $MoCl_4$ showed it to be identical with the $MoCl_4$ obtained by Schafer, *et al.*,[17] and Couch and Brenner.[16] The uncorrected molar susceptibility (temperature in parentheses) was found to be 1971×10^{-6} (297.9°), 3457×10^{-6} (152.9°), and 5727×10^{-6} (78.8°) cgs unit/mol. These values correspond to 2.36 BM ($\theta = -37°$) in good agreement with that of Schafer. Its far-infared spectrum was quite different from the low-temperature form showing a weak absorption at 240 cm^{-1}, a strong one at 300 cm^{-1}, and a strong doublet peak at 398 and 410 cm^{-1} with shoulders at 368 and 423 cm^{-1}.

Reduction of Tungsten Oxytetrachloride in Tetrachloroethylene.—A 1.9-g sample of freshly sublimed $WOCl_4$ was treated

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[22] B. N. Figgis and J. Lewis, "Technique of Inorganic Chemistry," H. B. Jonassen and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, pp 142–143.

with 20 ml of tetrachloroethylene in the same fashion as the WCl_6 reduction. After 60 hr the organic material was removed by distillation *in vacuo* and the excess $WOCl_4$ sublimed away at 175°. A 0.3-g amount of an olive green powder was obtained which represents 18% of theory for $WOCl_3$. An infrared spectrum of this material showed a single broad band centered at 784 cm^{-1} and an analysis of the X-ray powder diffraction data yielded lattic constants of a = 10.706 and c = 3.853 Å for a tetragonal unit cell. These results compare well with the data reported by Fowles and Frost[23] for $WOCl_3$. Gas chromatographic analysis of the organic material verified the presence of C_2Cl_6.

Niobium Pentachloride and Tantalum Pentachloride in Tetrachloroethylene.—A 1.00-g sample of $NbCl_5$ was treated with tetrachloroethylene in the same fashion discussed above. After 1 week the organic material was distilled away and the solid product was heated to 130° in a sealed tube, whereupon much $NbCl_5$ sublimed away leaving behind only 0.12 g of a brown powder (14% of theory for $NbCl_4$). Its X-ray powder diffraction pattern was identical with that of $NbCl_4$.[18] Gas chromatographic analysis of the organic material verified the presence of C_2Cl_6.

A 1.00-g sample of $TaCl_5$ did not react after 2 weeks.

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The Circular Dichroism of Tris(*l*-cyclohexanediamine)nickel(II) Chloride[1a]

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A discussion of the optical activity of coordination compounds in terms of the electronic structure of the metal ion was first presented by Moffitt in 1956.[2] Subsequent theoretical treatments by Piper and Karipides[3] and by Liehr[4] suggested specific crystal field or molecular orbital models for determining electric and magnetic transition moments. McCaffery and Mason performed empirical calculations of these quantities[5] and proposed a criterion for determining the absolute configuration of certain complexes based on a correlation of their circular dichroism behavior.[6]

The metal ions most extensively studed by these and later workers have been of the d^3 or d^6 configuration. The d^8 configuration of Ni(II) is of potential theoretical interest because it has three, rather than two, spin-allowed d–d bands in an octahedral field. Unfortunately, only a limited number of Ni(II) complexes have been found to be capable of resolution. They have been listed in a recent review.[7] A further problem encountered with Ni(II) is that its d–d bands do not all fall within the region of the spectrum commonly accessible to ORD and CD instruments.[8]

The complex ion, $Ni(l\text{-chn})_3^{2+}$, is not subject to racemization because its optical activity is inherent in the ligands.[9] This note reports its CD spectrum from 1200 to 300 mμ and endeavors to show that the rotational strengths of the three d–d transitions, as well as some other features of the CD spectrum, can be explained by present theory.

Experimental Section

Resolution of the ligand has been described previously.[10] To prepare the complex, nickel chloride (0.022 mol) was added to a solution of *l*-chn (0.074 mol) in 250 ml of water. The volume was reduced to 175 ml by boiling. Orchid crystals appeared upon cooling. Recrystallization from hot water gave the final product $[Ni(l\text{-chn})_3]Cl_2 \cdot 3H_2O$. *Anal.* Calcd for $NiC_{12}H_{48}N_6Cl_2O_3$: C, 41.08; H, 9.19; N, 15.97. Found: C, 41.20; H, 9.07; N, 15.99.

The absorption spectrum was determined on a Cary Model 14 RI spectrophotometer. Circular dichroism was measured on an instrument constructed in this laboratory by Professor Denning.[11]

Results and Discussion

The ligands of $Ni(l\text{-chn})_3^{2+}$ are bound as bidentate chelates in the manner of ethylenediamine. The absorption spectrum of the complex (Figure 1) has the three d–d bands typical of octahedrally coordinated Ni(II) indicating approximate O_h symmetry. As a result of the chelate rings, the actual symmetry is D_3. The CD spectrum reveals optical activity in all three absorption bands, but not to the same degree. This behavior can be explained on the basis of magnetic-dipole selection rules.[2] Thus, the low-energy band ($^3A_{2g} \rightarrow {}^3T_{2g}$) is the only one of the three transitions which is magnetically allowed in the O_h approximation. Correspondingly, it has the most intense circular dichroism. On the other hand, the moderately dichroic second band ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$) becomes allowed only through mixing with $^3A_{2g} \rightarrow {}^3T_{2g}$ under the actual, D_3, field. Finally, the third band ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) is only weakly dichroic since it is magnetically forbidden unless configuration interaction is considered.[4] It is a two-electron transition in the strong-field limit and a transition between different terms ($^3F \rightarrow {}^3P$) in the weak-field limit.

A further interesting feature of the CD spectrum is revealed if the disposition of the ligands around the

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(1) (a) Taken from the Ph.D. thesis of Richard S. Treptow, University of Illinois, 1966; (b) Miami Valley Laboratories, The Procter & Gamble Co., Cincinnati, Ohio 45239.

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