

A New Isomer of Molybdenum(IV) Chloride

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Received April 27, 1977

Introduction

α - MoCl_4 , prepared by treating MoCl_5 with boiling tetrachloroethylene, is isomorphous with NbCl_4 [1, 2]. The structure of the latter compound shows that it contains metal-metal bonds running through chains of linked octahedra [3]. While NbCl_4 is diamagnetic, α - MoCl_4 shows a very weak paramagnetism which suggests that metal-metal bonding occurs in MoCl_4 , but it is weak in comparison to that in NbCl_4 . A second isomer β - MoCl_4 , formed by reduction of MoCl_5 at higher temperatures [4, 5], exhibits higher magnetic moments (2.31–2.54 B.M.) which are normal for Mo^{4+} in an octahedral environment [6]. Technetium tetrachloride has normal magnetic behaviour [7] and its structure reveals no metal-metal bonding [8].

One method for preparing MoCl_4 involves heating MoO_2 in a stream of nitrogen laden with carbon tetrachloride vapour [9]. We have found that the magnetic properties of this material differ markedly from those of the compound when it is prepared by the other methods.

Experimental

Reagents

MoO_2 (99.9%) was supplied by Research Organic/Inorganic Chemical Co. The carbon used was Norit A and the CCl_4 was spectro-quality (Matheson Coleman and Bell). High purity nitrogen was passed through columns containing hot copper turnings and phosphorus pentoxide.

Preparation of MoCl_4

MoO_2 mixed with carbon was heated at 300 °C in a stream of nitrogen which had been saturated with carbon tetrachloride. Shchukarev's procedure [9] was modified slightly by substitution of a glass spiral for the water-cooled condenser at the exit end of the apparatus. This was much more effective in catching the fine particles of tetrachloride which were otherwise lost by being swept out of the system. The spiral was mounted vertically so that by gentle tapping the product could be made to fall into a receiver at the bottom. Temperatures in excess of 300 °C led to the

formation of trichloride and low temperatures resulted in contamination of the product with oxychloride. Pentachloride, also formed, was readily removed by sublimation *in vacuo* at 100 °C. The yield of tetrachloride from 5 g of reaction mixture was about 2 g. The mixture became caked and relatively unreactive after about 2 hr of heating. The product was soluble with hydrolysis in water and dissolved in ethanol and acetone but it was insoluble in benzene, ether and carbon tetrachloride. Traces of MoCl_3 were easily detected, if present, as an insoluble residue when the product was dissolved in ethanol. *Anal.* Calcd. for MoCl_4 : Mo, 40.35; Cl, 59.65. Found: Mo, 40.41; Cl, 59.70.

X-ray Diffraction

Powder diffraction data was obtained using $\text{CuK}\alpha$ radiation and a 11.5 cm diameter camera. Potassium chloride was used as an internal standard. It was found necessary to avoid vigorous grinding as isomerization to α - MoCl_4 occurred.

Magnetic Susceptibility Measurements

A Gouy balance was used employing fields up to 5200 gauss. The sample temperature was controlled to $\pm 1^\circ$. Diamagnetic corrections were applied using the values tabulated by Selwood [10].

Differential Thermal Analysis

DTA curves were obtained for samples of α - and β - MoCl_4 and the material prepared by Shchukarev's method sealed under vacuum in quartz ampoules which had a re-entrant thermocouple well. The sample was covered with a layer of powdered quartz which served as a radiation shield. This was necessary in order to protect the sample during the sealing operation. Immediately prior to sealing, the sample was cooled in liquid nitrogen.

Results and Discussion

The physical properties of the substance prepared by Shchukarev's method differed from those of α - and β - MoCl_4 . The principal difference is seen in the magnetic behavior. Susceptibility and effective magnetic moment values for two preparations designated I and II are given in Table I. The values of μ_{eff} increase slightly with temperature. This conforms to the expected behavior for an ion in an octahedral field in a $^3T_{1g}$ state [11].

The β -isomer exhibits a magnetic moment of 2.31–2.54 B.M. [5]. The susceptibility obeys a Curie-Weiss Law, *i.e.* $\mu_{\text{eff}} = 2.86 \sqrt{\chi_M(T - \theta)}$, with $\theta = -37$ to -39°C . This indicates that there is exchange interaction between neighboring cations but no

TABLE I. Magnetic Susceptibility Data for Various Preparations of MoCl₄.

Sample	T °K	χ_M (corrected) $\times 10^6$	μ_{eff} (B.M.)
Preparation I	298	1512	1.91
	274	1615	1.89
	253	1727	1.88
	193	2282	1.88
	143	3037	1.87
Preparation II	300	1527	1.92
	242	1820	1.88
	186	2259	1.84
	168	2457	1.82
Preparation I heated to 150 °C	298	229	0.74
	258	246	0.72
	218	270	0.69
	166	308	0.64
	120	342	0.61
Preparation II heated to 150 °C	298	234	0.75
	278	243	0.74
	246	262	0.72
	227	269	0.70
	175	311	0.66
	133	349	0.61

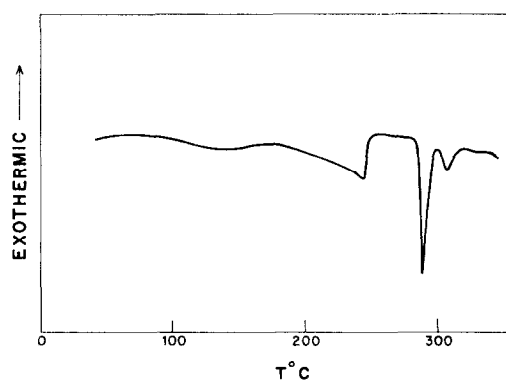
metal-metal bonding. Preparations I and II very nearly obeyed the Curie law with $\theta = 2$ to -7 °C. There is therefore no appreciable exchange interaction. We shall hereafter refer to the Shchukarev product as the γ -isomer.

The γ -isomer was heated *in vacuo* at 130 °C for several hours but no change in magnetic properties was observed. Heating for 5 hr at 150 °C caused a marked decrease in magnetic susceptibility as may be seen in Table I. The moments so obtained are in fair agreement with those obtained by Kepert and Mandy-czewsky for α -MoCl₄ [2]. When the γ -isomer was heated to 250 °C, the X-ray diffraction pattern of the product was identical to that for the β -isomer. It has been shown previously that α -MoCl₄ is converted to β -MoCl₄ at elevated temperatures [1].

We located the transition temperatures for the changes $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \beta$ by differential thermal analysis. The DTA curve of γ -MoCl₄ is shown in Figure 1. A broad endothermic band centred near 140 °C is apparently due to the $\gamma \rightarrow \alpha$ transition. The sharper band at 241 °C is ascribed to the $\alpha \rightarrow \beta$ transition. A strong band at 288 °C which appeared in the curves of all three isomers is believed to result from the endothermic (8 kcal mol⁻¹) process:



In order to confirm the assignment, we calculated the pressures of MoCl₅ vapor which would result from heating MoCl₄. ΔH_f° and ΔS_f° for the three sub-

Fig. 1. Differential thermal analysis curve for γ -MoCl₄.TABLE II. X-ray Powder Diffraction Data for γ -MoCl₄ and α -MoCl₄. The d -spacings are in angstroms. Intensity estimates appear in brackets.

γ -MoCl ₄	α -MoCl ₄
	9.092 (5)
6.695 ± 0.003 (50)	6.099 (100)
	5.888 (100)
5.367 ± 0.014 (100)	5.383 (5)
5.092 ± 0.010 (20)	5.091 (10)
4.837 ± 0.010 (20)	4.866 (10)
4.595 ± 0.003 (20)	4.618 (10)
4.394 ± 0.002 (100)	4.386 (5)
4.059 ± 0.004 (50)	4.042 (80)
3.537 ± 0.003 (50)	
3.249 ± 0.003 (40)	3.266 (30)
3.029 ± 0.002 (60)	
2.879 ± 0.002 (60)	2.856 (30)
	2.632 (100)
2.542 ± 0.001 (50)	2.522 (25)
2.442 ± 0.001 (70)	2.491 (2)
2.318 ± 0.007 (10)	2.320 (2)
	2.221 (50)
	2.181 (20)
2.210 ± 0.000 (30)	2.131 (20)
2.115 ± 0.002 (40)	2.102 (50)
2.062 ± 0.009 (30)	2.075 (1)
1.936 ± 0.000 (30)	1.897 (5)

stances which appear in the above equation were taken from the work of Shchukarev *et al.* [12].

A further peak appeared in the DTA curve at 305 °C. This was possibly due to the transition $\beta\text{-MoCl}_{3.08} \rightarrow \alpha\text{-MoCl}_3$. Schäfer *et al.* [5] have shown that low temperature decomposition of higher molybdenum chlorides following the method of Colton and Martin [14] appears to yield $\beta\text{-MoCl}_{3.08}$ while $\alpha\text{-MoCl}_3$ is formed at higher temperatures. The assignment of this peak is left as tentative because it was not our object to examine the MoCl₃ phase.

X-ray data on γ -MoCl₄ were recorded by averaging several measurements of each line spacing. The d -

spacings are listed in Table II. As the degree of crystallinity of the finely powdered material was not high large angle reflections were not observed. Average deviations in the measurement of d -spacings are given for each line of γ -MoCl₄ and these are followed by line intensities estimated visually. The d -spacings for α -MoCl₄ reported by Kepert and Mandyczewsky [2] in most cases approximate those which we have observed. There is total disagreement at the smallest angles and there is little correspondance in intensities. The average deviations in the spacings for γ -MoCl₄ are usually much less than the differences in spacings for α - and γ -MoCl₄ respectively.

We conclude that γ -MoCl₄ is closely analogous to α -MoCl₄ except that the metal-metal bonding is absent. This would account for the absence of strong lines due to heavy atom reflections in γ -MoCl₄. If the coupling of metal atoms to form Mo-Mo bonds entails an activation energy, the substance formed from the vapor phase at the lowest temperatures could indeed contain chlorine bridges without metal-metal bonds. The need for an energy of activation is reasonable as the bridging chlorine bond angles would have to be distorted in order for the metal atoms to approach one another. The broadness of the DTA peak is also reasonable because if the metal-metal bond formation does not proceed "domino-fashion" down the chains of octahedra but rather occurs randomly, a great deal of disorder would result. It could require considerable time to rearrange the bonding to give an ordered structure.

Acknowledgment

The authors wish to thank the National Research Council for financial support.

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