NOTES

1221. *The Paramagnetism of Some Molybdenum Complexes*

By J. H. Garside

THIS Note reports the magnetic susceptibilities of a series of molybdenum(V) oxychlorides and oxybromides. With the exception of some isolated determinations, referred to later, magnetic studies of these compounds have been confined to single-temperature measurements.[1,2] In the present investigation the magnetic susceptibilities were measured over the range 90—300°K.

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[1] W. Klem and H. Steinberg, *Z. anorg. Chem.*, 1936, **227**, 198; P. Ray, *J. Indian Chem. Soc.*, 1930, **7**, 741; B. T. Tjabbes, *Proc., k. ned. Akad. Wetenschap.*, 1932, **35**, 693.

[2] E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J.*, 1963, 4649.

One general feature (see Table) is that the values of magnetic moment at 300°K are close to the spin-only value of 1·73 B.M. for one unpaired electron. This is in agreement with previous measurements[2] of similar compounds and is consistent with the quenching of the orbital contribution by the magnetic field. The inverse corrected molar susceptibility, plotted against temperature, in each case gave a straight line with an intercept of θ (Figures 1 and 2). The values of θ are not sufficiently large seriously to affect the magnetic moment at 300°K. The values of θ are greater for the ammonium and

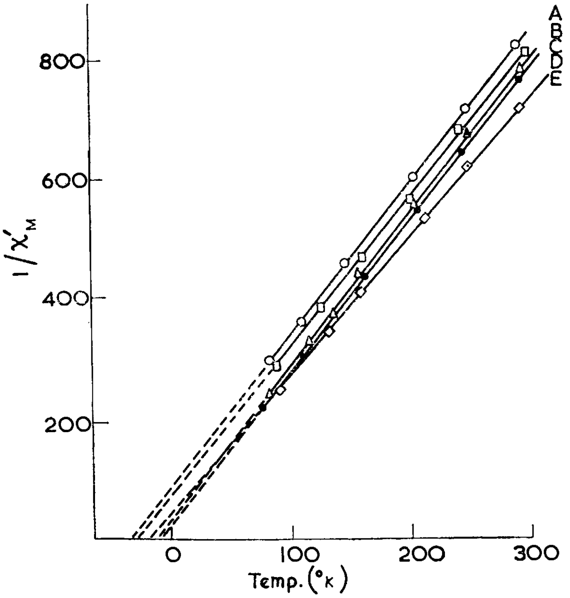

FIGURE 1

A, K_2MoOCl_5
B, $(NH_4)_2MoOCl_5$
C, $(C_5H_6N)_2MoOCl_5$
D, $(C_9H_8N)MoOBr_4$
E, $(C_5H_6N)_2MoOBr_5$

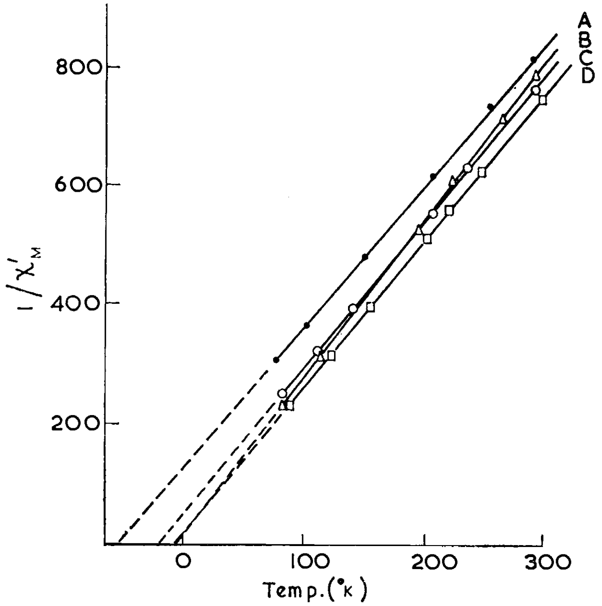

FIGURE 2

A, $(NH_4)_2MoOBr_5$
B, $(C_9H_8N)_2MoOCl_5,H_2O$
C, $(C_5H_6N)MoOBr_4$
D, $(C_9H_8N)_2MoOBr_5$

potassium salts, which are less magnetically dilute, than for the corresponding pyridinium and quinolinium salts. However, in the absence of any definite indication of antiferromagnetic interactions no particular significance can be attached to θ. It has been established that the strong multiple bonding between the molybdenum and oxygen atoms reduces the spin–orbit coupling constant from 1030 to 240 cm.$^{-1}$. The behaviour of compounds reported in this Note confirms such a reduction.

The work of Sacconi and Cini[3] prompted the study of the magnetic behaviour of diammonium molybdenyl oxychloride in hydrochloric acid and diquinolinium molybdenyl oxybromide in hydrobromic acid. These compounds in particular were chosen for their somewhat greater stability and consequent ease of handling. In Figure 3 are plotted the values of corrected molar susceptibility of solute against acid concentration. In the first case, at concentrations of hydrochloric acid greater than 6·5M, χ'_{M} approaches the value for the solid. Below 6·5M, χ'_{M} decreases and finally approaches the value obtained in aqueous solution, *i.e.*, $86{\cdot}5 \times 10^{-6}$. This residual paramagnetism is more likely to be the result of a small temperature-independent paramagnetic effect associated with the formation of the diamagnetic dimer[4] in aqueous solution than the presence of monomeric ions. Electron spin resonance measurements[5] have shown the absence of paramagnetic species in hydrochloric acid solutions of strength less than 2M. Recent studies[5,6] have indicated the formation of a paramagnetic dimer in 6M—10M-solutions prior to diamagnetic dimerisation in weaker acid solution. Such behaviour would not be indicated by susceptibility measurements unless a change occurred in the number of unpaired electrons.

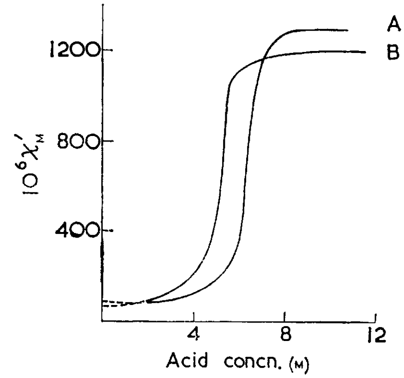

FIGURE 3. A, Solutions of $(C_9H_8N)_2MoOBr_5$ in HBr.
B, Solutions of $(NH_4)_2MoOCl_5$ in HBr

The behaviour of the molybdenyl oxybromide in hydrobromic acid follows very closely that of the chloride. Again values of χ'_{M} in weak acid solution approach the value in aqueous solution of $78{\cdot}6 \times 10^{-6}$. There was no indication that the paramagnetism in strong acid solution was due to species other than $[MoOBr_5]^{2-}$. However the existence of $[MoOBr_4]^-$ species in solution is indicated by the precipitation of the red crystalline compounds $[C_9H_8N]MoOBr_4$ and $[C_5H_6N]MoOBr_4$ in solutions of HBr greater than 11M.

Spectrophotometric studies[2,6,7] of the equilibria of molybdenum(V) in acid solution have revealed the presence of a large number of species. Correlation between this work, magnetochemical, and electron spin resonance studies is uncertain because of the great differences in the molybdenum concentrations used. The results of spectrophotometric studies of solutions of molybdenum(V) concentrations comparable with those used in the present work will be considered in a subsequent Communication.

[3] L. Sacconi and R. Cini, *J. Amer. Chem. Soc.*, 1954, **76**, 4239.
[4] C. M. French and J. H. Garside, *J.*, 1962, 2006.
[5] C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 831.
[6] G. P. Haight, jun., *J. Inorg. Nuclear Chem.*, 1962, **24**, 663.
[7] P. C. H. Mitchell, *J. Inorg. Nuclear Chem.*, 1963, **25**, 963.

Experimental.—Magnetic susceptibilities were measured by the Gouy method with aqueous nickel chloride as the standard.[8] The electromagnet was a copy of that designed by Bates and Lloyd-Evans.[9] Temperature variation was obtained by simultaneous cooling with liquid nitrogen and controlled heating. The temperature of the sample chamber was measured with thermocouples sealed into the apparatus at points corresponding to the ends of the specimen tube. At thermal equilibrium the temperature gradient along the sample chamber was less than 0·1° per cm. All the compounds were measured in the finely divided solid state; French and Harrison's equation,[10] modified for a nitrogen atmosphere, was used for calculation of susceptibility. Measurements were also made on aqueous and acid solutions of some of the complexes. Plots of the susceptibility of the solution against the weight fraction of solute were linear, and for aqueous solutions values of the specific susceptibility extrapolated to infinite dilution were in good agreement with the accepted value for water, confirming the validity of Wiedemann's law for these solutions. The slopes of these graphs gave acceptable values for the specific susceptibility of the solutes.

						Magnetic moment		
Compound *	Density	−Diamag. (corr.)	$10^6\chi_S$ (293°K)	$10^6\chi_M$ (293°K)	$10^6\chi'_M$ (293°K)	(300°K)	(90°K)	(θ)
K_2MoOCl_5 ………	2·551	189	2·956	1086	1275	1·74	1·60	27°
$(NH_4)_2MoOCl_5$ …	2·203	208	3·140	1021	1229	1·71	1·54	32
Q_2MoOCl_5,H_2O …	1·634	344	1·637	929·4	1273	1·74	1·71	4
Py_2MoOCl_5 ……	1·799	259	2·265	1018	1277	1·74	1·66	15
$(NH_4)_2MoOBr_5$ …	3·063	279	1·768	967·9	1247	1·72	1·48	51
Py_2MoOBr_5 ……	2·436	330	1·596	1072	1402	1·82	1·71	17
Q_2MoOBr_5 ………	2·158	402	1·227	947·0	1349	1·80	1·76	6
$PyMoOBr_4$ ……	1·575	240	2·105	1077	1317	1·76	1·66	16
$QMoOBr_4$ ………	2·520	277	1·838	1033	1310	1·76	1·71	9

* Py = pyridinium; Q = quinolinium.

Densities of solids were calculated from the weight of benzene displaced from a specific-gravity bottle by a known weight of the compound.

The molybdenyl pentachlorides and pentabromides were prepared from molybdenum(v) solutions by the methods[11] of James and Wardlaw, and of Angell, James, and Wardlaw. The tetrabromide compounds were prepared by treating the corresponding pentabromides with 60% hydrobromic acid. Microanalyses were performed in all cases, to verify the purity of the compounds. In view of their sensitivity to air and moisture the compounds were always handled in a dry-box in an atmosphere of nitrogen.

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[8] H. R. Nettleton and S. Sugden, *Proc. Roy. Soc.*, 1939, *A*, **173**, 313.

[9] L. F. Bates and A. Lloyd-Evans, *Proc. Phys. Soc.*, 1933, **45**, 425.

[10] C. M. French and D. Harrison, *J.*, 1953, 2538.

[11] R. G. James and W. Wardlaw, *J.*, 1927, 2145; F. G. Angell, R. G. James, and W. Wardlaw, *J.*, 1929, 2578.