374. *The Diamagnetism of Some Molybdenum Complexes.*

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Several complex oxalates of molybdenum in the 4+, 5+, and 6+ valency states, molybdenyl bisacetylacetonate, and three heteropolymolybdates are found to be diamagnetic but with an underlying temperature-independent paramagnetism. The structural conclusions are outlined.

ALTHOUGH the magnetic behaviour of compounds of molybdenum in its various valency states has been studied for a number of years, complexes containing this element have not received the extensive investigation of those of elements of the first transition series. The complexes of molybdenum in the 4+ and 5+ valency states might be expected to be paramagnetic by virtue of the unpaired 4*d*-electrons, but those of molybdenum(6+), with no unpaired 4*d*-electrons, should be diamagnetic. With the exception of some complex molybdenum halides which will be considered in a subsequent paper, the compounds of molybdenum(IV) studied magnetochemically are restricted largely to potassium octacyanomolybdate(IV) $K_4Mo(CN)_8$ and its dihydrate,[1,2] and potassium pentacyanomolybdate $KMo(CN)_5$,[3] all of which are diamagnetic. The diamagnetism is ascribed to d^4sp^3-hybridisation, giving rise to eight-covalent bonds in the first two compounds and to the formation of an " inner orbital " type of complex in the third case. Similarly, with molybdenum(V), magnetochemical measurements on compounds other than halides are confined largely to potassium octacyanomolybdate(V) $K_3Mo(CN)_8$,[2] which as expected, exhibits a paramagnetism corresponding approximately to one unpaired electron, and the binuclear and hence diamagnetic cyclopentadienylmolybdenum.[4] Finally, a number of molybdenum(VI) compounds have been studied,[5] and as expected all are diamagnetic or exhibit only a very small paramagnetism, as do also various polymolybdates.[6] However, little systematic work on series of molybdenum compounds has been carried out, and the following represent an amplification of existing results.

EXPERIMENTAL

Magnetic susceptibilities were measured by the Gouy method and apparatus, with benzene ($\chi_s = 0{\cdot}702 \times 10^{-6}$ c.g.s unit) as the standard. The electromagnet was a copy of that designed by Bates and Lloyd-Evans [7] and was used with a pole-gap of 2 cm. and an exciting current of 2 amp. All the compounds were measured at room temperature, in the finely divided solid state; French and Harrison's equation [8] was used for calculation of susceptibility. Whenever the complex was sufficiently water-soluble, measurements were also made on solutions at a series of concentrations. Plots of the susceptibility of the solution against the weight fraction of solute were linear, and extrapolated values of the specific susceptibility of water were in good agreement with the accepted value, confirming the validity of Wiedemann's law in these cases. The slopes of these graphs gave a value for the specific susceptibility of the solute in each case. Measurements were also carried out on some complexes at low temperatures in a cryostat cooled in liquid nitrogen.

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

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[1] Ray and Bhar, *J. Indian Chem. Soc.*, 1928, **5**, 497; Biltz, *Z. anorg. Chem.*, 1928, **170**, 161; Klemm and Steinberg, *ibid.*, 1936, **227**, 193.

[2] Rawlinson, *Austral. Chem. Inst. J. Proc.*, 1941, **8**, 42.

[3] Steele, *Austral. J. Chem.*, 1957, **10**, 404.

[4] Wilkinson, *J. Amer. Chem. Soc.*, 1954, **76**, 209.

[5] Tjabbes, *Proc. Acad. Sci. Amsterdam*, 1932, **35**, 693; Beckmann and Zocher, *Z. phys. Chem.*, 1926, **124**, 318; Tilk and Klemm, *Z. anorg. Chem.*, 1939, **240**, 355; St. Meyer, *Wied. Annalen*, 1899, **66**, 698; *Ann. Phys.*, 1899, **69**, 236; Klemm, Jacobi, and Tilk, *Z. anorg. Chem.*, 1931, **201**, 1.

[6] Das and Ray, *J. Indian Chem. Soc.*, 1944, **21**, 159.

[7] Bates and Lloyd-Evans, *Proc. Phys. Soc.*, 1933, **45**, 425.

[8] French and Harrison, *J.*, 1953, 2538.

The oxalates were prepared by Spittle and Wardlaw's method,[9] and molybdyl bisacetylacetonate by Morgan and Castell's method;[10] the heteropolymolybdates were commercial specimens. Microanalyses were performed in all cases to check 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 dry nitrogen.

RESULTS

The physical data including the magnetic susceptibility results are shown in the Table. Values of the inherent diamagnetism shown in column 4 were calculated by Slater's formula.[11]

Compound *	Oxidn. state	d	−Diamag. (corr.)	$-10^6\chi_s$	$-10^6\chi_M$	$10^6\chi'_M$	Δ
$K[MoO_2(Ox)],1{\cdot}5H_2O$	5	2·702	106·3	$0{\cdot}209_1$	58·90	47·4	47·4
$NH_4[MoO_2(Ox)],1{\cdot}5H_2O$ ...	5	1·999	115·9	$0{\cdot}201_6$	52·62	63·3	63·3
$Ba[MoO_2(Ox)]_2,5H_2O$	5	2·781	243·4	$0{\cdot}229_3$	151·2	92·2	46·1
$Q[MoO_2(Ox)],H_2O$	5	1·940	170·3	$0{\cdot}360_4$	127·4	42·9	42·9
$Py_3H[Mo_4O_8(Ox)_4],6H_2O$ ...	5	1·972	526·7	$0{\cdot}286_7$	347·8	178·9	44·7
$K_2[Mo_3O_4(Ox)_3],5H_2O$	4	1·621	307·6	$0{\cdot}182_4$	131·1	176·5	58·8
$Py_2[Mo_3O_4(Ox)_3],5H_2O$	4	1·393	377·2	$0{\cdot}236_9$	205·3	171·9	57·3
$Q_2[MoO_2(Ox)_2]$	6	1·730	264·8	$0{\cdot}360_7$	203·4	61·4	61·4
$MoO_2(CH_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CH_3)_2$	6	1·640	121·4	$0{\cdot}270_3$	79·5	41·9	41·9
$Na_4SiMo_{12}O_{40}$	6	3·510	687·8	$0{\cdot}063_7$	121·8	566·0	47·2
$Na_3PMo_{12}O_{40}$	6	3·252	682·2	$0{\cdot}062_2$	117·6	564·6	47·0
$Na_8P_2Mo_{18}O_{62}$	6	3·149	1058·0	$0{\cdot}097_5$	284·6	773·4	42·9

* Ox = $H_2C_2O_4$; Py = pyridinium; Q = quinolinium.

DISCUSSION

Of the compounds in the present series, only the barium salt had been previously studied magnetochemically, and the current value of magnetic susceptibility agrees well with that of $-0{\cdot}23 \times 10^{6}$ c.g.s. units at 18° obtained by Tjabbes.[5]

One general feature (see Table) is that after correction for inherent diamagnetism a small paramagnetism (χ'_M) remains for each compound. Measurements on several compounds at liquid nitrogen temperature show the susceptibility to be unchanged within the limits of experimental error at the lower temperature (*e.g.*, -10^6 χ_s for $Ba[MoO_2(C_2O_4)]_2,5H_2O$ is 0·2319 at 82·9° K, and 0·2293 at room temperature). The residual paramagnetism is thus temperature-independent.

None of the five molybdenum(V)–oxalate complexes exhibits the temperature-dependent paramagnetism expected from the one unpaired electron of molybdenum in this valency state. The observed behaviour may be attributed to the existence of these compounds in the dimeric state with consequent interaction of the electron spins on neighbouring molybdenum atoms, which removes the paramagnetism. Evidence in support of some form of polymerisation of these compounds in solution of concentration greater than 8% has been adduced by Wardlaw and Spittle[9] from cryoscopic measurements, although for concentrations less than 0·9% molecular weights corresponding to the monomeric formula were obtained. Accurate molecular weights proved impossible to determine in the present work owing to the thermal instability of the compounds and their insolubility in solvents suitable for cryoscopic measurements. *X*-Ray powder photographs also failed to give data of use for this purpose, owing to the low symmetry of the complexes and the impossibility of obtaining single large crystals. The smallness of the forces operating makes magnetic measurements on solutions of concentration less than 1% impracticable, but no indication of monomeric ions was obtained from such measurements down to this concentration. The structure suggested by Wardlaw and Spittle, and shown in (A), for the large anion in the first four of the molybdenum(V) oxalates in the

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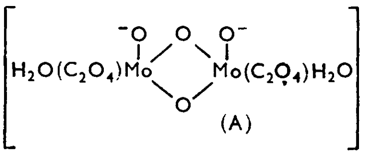
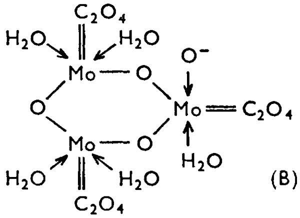
[9] Spittle and Wardlaw, *J.*, 1928, 2742; 1929, 792; 1931, 1748.
[10] Morgan and Castell, *J.*, 1928, 3252.
[11] Slater, *Phys. Rev.*, 1930, **36**, 57.

Table would account for the observed magnetic behaviour of the solid compounds also. The existence of the various hydrates that may be obtained with one or more molecules of water per molybdenum atom would not affect the general pattern of magnetic behaviour.



(A)



(B)

Analysis of the pyridinium salt of the oxalatomolybdenum(V) complex corresponded to the empirical formula $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4],6H_2O$. This compound may be formulated in the same way as the previous four if the diamagnetism is again assumed to be accounted for by Mo–Mo interaction in the dimer.

The two complexes of molybdenum(IV) are also diamagnetic, and, as seen from the Table, exhibit a temperature-independent paramagnetism a little greater than that of the molybdenum(V) compounds. They fail, however, to show the normal paramagnetism expected from two unpaired electrons. These results are not incompatible with the suggestions of Wardlaw and Spittle[9] who considered the compounds to be salts of an acid with the ring structure in which three molybdenum atoms are linked by oxygen atoms, the complex anion having structure (B). Interaction between unpaired electrons associated with neighbouring molybdenum atoms in delocalised orbitals above and below the plane of the 6-membered ring may be postulated, and this will account for the disappearance of the expected paramagnetism.

The various complexes of molybdenum(VI) exhibit the expected diamagnetism, but again the appearance of a temperature-independent paramagnetic term after treatment of the experimental data as before is worthy of note.

Finally, the same general pattern of magnetic behaviour is obtained in the case of the heteropolymolybdates as for the other compounds studied in this work. While the exact structure of the various heteropolymolybdates that can be obtained is still uncertain, *X*-ray evidence has confirmed the existence of octahedral MoO_6 groups and their linkage through oxygen bridges in large ring-shaped structures. The present magnetochemical data are not incompatible with this, but in the absence of more precise structural information further speculation would be unjustifiable.

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