

NOTES

Co-ordination Chemistry of Quinquevalent Molybdenum-
Reactions of Oxohalomolybdates (V)

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Sand and Burger¹ isolated a copper-red solid from $(P_yH)_2 [MoOCl_5]$ by ethanolysis which has been later on shown to be diamagnetic by Klemm². The constitution of this compound has been the subject of immense interest to different authors. Sand and Burger formulated it as $Mo(OH)_3Cl_2 \cdot C_6H_5N$ although their analytical data did not strictly correspond to this formula. Later on, James and Wardlaw³ formulated it as a salt, $(P_yH)[MoO_2Cl_2(H_2O)]$, although, they gave a different formula to their own compound $(P_yH)[MoO_2Cl_2] \cdot 0.25 H_2O$ isolated by them. Since it is now known that feeble paramagnetism or diamagnetism of quinquevalent molybdenum compounds can be better explained on the basis of oxobridged bi-nuclear species like $Mo_2O_4^{2+}$ and $Mo_2O_3^{4+}$ with a possible metal—metal interaction, the formulation of Sand and Burger's compound mentioned above seems to be incompatible. We have recently studied the compound by spectroscopic and conductivity measurements in aqueous and nonaqueous media and we have seen that in aqueous solution the compound undergoes extensive hydrolysis and ionisation.

Recently, we have carried out similar reactions with $(P_yH)_2[MoOBr_5]$ and $(P_yH)[MoOBr_4]$ and we have isolated in both these cases, an identical diamagnetic copper-red compound the analytical composition of which closely corresponds to $[Mo_2O_2(OH)_2Br_4P_{y2}]$. We have isolated a new compound $(P_yH)[MoOBr_3(acac)]$ a paramagnetic brown solid by similar reaction in presence of acetylactone. Analytical methods used in these cases are similar to our previous communication⁴. Quinquevalency of molybdenum has been established by modified ceric sulphate titration and magnetic measurements have been done by Gouy method. The results are tabulated in Table I.

TABLE I

Compound	Mo(%)		Br(%)		N(%)		μ_{eff} (B.M.) at 30°
	Found	Calc.	Found	Calc.	Found	Calc.	
$[Mo_2O_2(OH)_2Br_4P_{y2}]$ copper-red crystals.	26.10	26.08	43.34	43.45	3.66	3.80	0.44
$(P_yH)[MoOBr_3(acac)]$ Reddish brown shining crystals.	18.18	18.04	45.66	45.10	3.32	2.63	1.84

1. J. Sand and O. K. H. Burger, *Ber.*, 1906, **39**, 176.
2. W. Klemm and H. Steinberg, *Z. anorg. Chem.*, 1936, **227**, 193.
3. R. G. James and W. Wardlaw, *J. Chem. Soc.*, 1927, 2145.
4. H. K. Saha and A. K. Banerjee, *Jour. Indian Chem. Soc.*, 1968, **15**, 660.

Considering the coordination number of molybdenum to be six in the copper red diamagnetic solid we suggest the following structure (Fig. 1) for our compound as well as of Sand and Burger's compound,

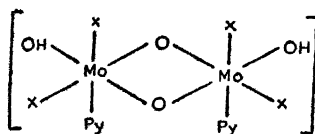


Fig 1

where X = Br or Cl

However, the salt like nature as suggested by James and Wardlaw³ and the subsequent hydrolysis and ionisation as evidenced by their conductivity measurements and also of ours may be explained by the following steps of reactions in aqueous solution (Fig. 2).

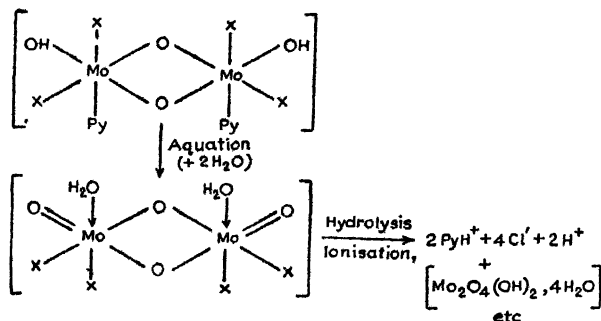


Fig 2.

Further investigations of these reactions and products are in progress which will be reported later.

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