

AN OXALATO COMPLEX OF MOLYBDENUM $(\text{NH}_4)_4\text{Mo}(\text{OX})_4 \cdot 8\text{H}_2\text{O}^*$

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The oxalato trichelate salt $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3$ is well known, but attempts to form a similar molybdenum compound have failed. Foerster and Fricke (1923) tried to produce an oxalate by dissolving $\text{Mo}(\text{OH})_3$ in oxalic acid. Spittle and Wardlaw (1929), following the earlier methods of Chilesotti (1906), also tried to produce an oxalate with reduced molybdenum.

It seemed probable, however, that if the molybdenum was reduced electrolytically in the presence of the cation there would be a greater possibility of producing a complex of the type R_4MoOX_4 . This procedure was found to be effective.

The complex is diamagnetic and like the octacyanides it is probable that the bond orbitals used in its formation are $4d^45s5p^3$.

Experimental

Ammonium Tetraoxalato Molybdenum(IV) $(\text{NH}_4)_4\text{Mo}(\text{OX})_4 \cdot 8\text{H}_2\text{O}$.—Ammonium molybdate (10 g) and oxalic acid (20 g) were dissolved in water (250 ml). The solution was electrolysed using a sintered glass partition. The electrodes were a platinum anode and a mercury cathode ($1\frac{1}{2}$ in. dia.). The electrolysis proceeded at 24 V, 2–3 A for 12–14 hr. The initial colour of the electrolyte was clear and slightly brown. At the beginning of electrolysis the colour became a golden-yellow changing to yellowish brown, and thence to a reddish brown when evolution of hydrogen set in at the cathode.

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(the Mo(III) stage). The temperature rose to 75 °C during electrolysis and the final colour of the reduced electrolyte was red. The reduced electrolyte was removed from the cell without any protective atmosphere and was placed in the refrigerator for crystallization after filtration. (A small amount (1 to 2 g) of a brownish material of unknown composition separated. This was filtered off and washed with ethanol. Before washing with ethanol this precipitate began to change to a bluish colour on the surface as soon as the mother liquor had drained off.)

Ethanol was added to the filtrate and a yellowish brown precipitate formed. This precipitate was filtered off, washed with ethanol, and dried at 40 °C, yielding a light brown product (Found: Mo, 14.5; OX, 53.3; NH₄, 10.8 per cent. Calc. for (NH₄)₄Mo(OX)₄.8H₂O: Mo, 14.5; OX, 53.6; NH₄, 10.8 per cent).

The conductance for 10⁻³M is 730 mhos at 25 °C and this is comparable with the double salt (NH₄)₃MoCl₆.NH₄Cl.2H₂O, 730 mhos (Steele 1955).

The oxalato complex charred at 60 °C. It is very soluble in water, giving a reddish brown solution, but is insoluble in common organic solvents.

References

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