Preparation, Spectrum, and Substitution Properties of $Mo(H_2O)_6^{3+}$

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Summary Hexa-aquomolybdenum(III) has been prepared in aqueous acidic media, and the u.v. visible spectrum obtained; kinetic data for the formation of 1:1 complexes with Cl^- and NCS^- are consistent with an S_N2 mechanism.

The preparation of $Mo(H_2O)_6^{3+}$ in aqueous *p*-toluenesulphonic acid (HPTS) and trifluoromethylsulphonic acid media has been described.[1] Kustin and Toppen[2] have repeated the preparation in HPTS and have reported a spectrum with no peak at 297 nm, but with significant absorption at 293 nm (ϵ 370 l mol^{-1} cm^{-1}). We have now obtained the spectrum illustrated in the Figure with much lower absorption and with prominent *d–d* bands which correspond well with those for the well characterized complex $MoCl_6^{3-}$. The same spectrum >300 nm has been obtained in aqueous HBF_4 solutions.†

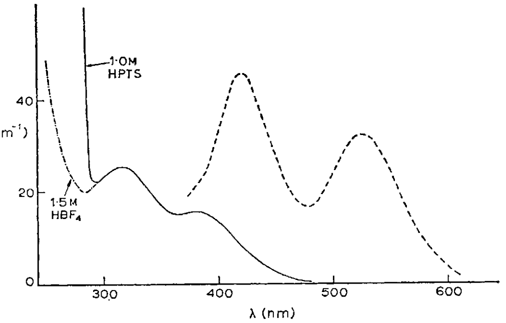
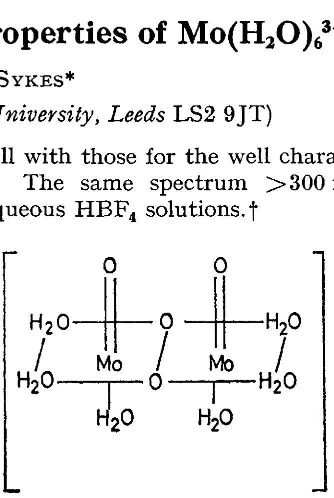


FIGURE. The spectrum of $Mo(H_2O)_6^{3+}$ (———) in aqueous 1·0M *p*-toluensulphonic acid (HPTS), and (—·—·) in 1·5M HBF_4. The absorption below 300 nm is due to the medium. A comparison is made with the spectrum of $MoCl_6^{3-}$ (- - -) in 12M HCl solution.



(I)

Our procedure is very like that described by Bowen and Taube.[1] Optimum conditions for the aquation of $MoCl_6^{3-}$ are with 0·0025M complex in 0·5M HPTS, and the time required for aquation is 2 days at room temperature. A cation ion-exchange resin Dowex 50W-X 12 (H^+ form) was used to separate the products. On elution with 0·5M HPTS the molybdenum(III) product was found to contain chloride. With 1M HPTS (or 1·5M HBF_4) the molybdenum product is free from chloride and consists of yellow $Mo(H_2O)_6^{3+}$. Further ion-exchange work on the $Mo(H_2O)_6^{3+}$ fraction indicated the presence of a single species. Rigorous air-free techniques are required at all times. Absorption peaks first reported by Bowen and Taube[1] are due to *ca.* 35% contamination by the di-μ-oxomolybdenum(V) dimer, the structure of which has recently been determined (I).[3] The absorption for $Mo(H_2O)_6^{3+}$ reported by Kustin and

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† Bowen and Taube (unpublished work) have repeated the preparation of $Mo(H_2O)_6^{3+}$ following observations made by Kustin and Toppen (ref. 2). The spectrum which they now obtain is in good agreement with our own. We are most grateful to Professor Taube for providing this information.

Toppen[2] at 293 nm is more than ten-times greater than we observed; the rate constant which they have reported for the reaction with thiocyanate differs by a factor of *ca.* 40, *assuming they* were working at 25°.

TABLE

Kinetic data for the 1:1 complexing of $Mo(H_2O)_6^{3+}$ with Cl^- and NCS^-, $I = 1{\cdot}0$M (LiPTS)

Anion	k_f (25°)/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
Cl^-	$(4{\cdot}60 \pm 0{\cdot}23) \times 10^{-3}$	$23{\cdot}5 \pm 0{\cdot}6$	$9{\cdot}6 \pm 2{\cdot}1$
NCS^-	$(2{\cdot}68 \pm 0{\cdot}13) \times 10^{-1}$	$16{\cdot}3 \pm 0{\cdot}4$	$-6{\cdot}4 \pm 1{\cdot}3$

Solutions of $Mo(H_2O)_6^{3+}$ have been kept under air-free conditions for over a week at 0° without serious deterioration. The ion reacts rapidly with oxygen; details were not investigated. It also reacts with perchlorate ions, but at a rate which is much faster than with V^{2+}, V^{3+}, Ti^{3+}, and Ru^{2+},[4] to give (I). The latter does not react with ClO_4^-, but is oxidized to molybdenum(VI) by chlorate ions.

The kinetics of the equilibrium (1) have been studied,

$$Mo(H_2O)_6^{3+} + Cl^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} M(H_2O)_5Cl^{2+} + H_2O \qquad (1)$$

$I = 1{\cdot}0$M (LiPTS), with chloride in large excess. Pseudo-first order rate constants, k_{eq}, determined spectrophotometrically can be expressed as in (2). Data for k_f are

$$k_{eq} = k_f[Cl^-] + k_b \qquad (2)$$

shown in the Table; at 25° $k_b = (4{\cdot}26 \pm 0{\cdot}12) \times 10^{-4}$ s^{-1}, $\Delta H^{\ddagger} = 12{\cdot}9 \pm 0{\cdot}6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30{\cdot}7 \pm 2{\cdot}1$ cal K^{-1} mol^{-1}. The formation constant for (1) is 10·8 l mol^{-1} at 25°. Complexing with thiocyanate is more extensive and the formation constant for (3) is *ca.* 10^5 l mol^{-1}. Rate

$$Mo(H_2O)_6^{3+} + NCS^- \xrightarrow{k_f} Mo(H_2O)_5NCS^{2+} + H_2O \qquad (3)$$

constants were obtained spectrophotometrically, molybdenum(III) in large excess, at λ_{max} 303 nm for $MoNCS^{2+}$ ($\epsilon = 2170$ l mol^{-1} cm^{-1}). Kinetic data for k_f, $I = 1{\cdot}0$M (LiPTS) are summarized in the Table.

The following observations support an S_N2 mechanism for the reaction of Cl^- and NCS^- with $Mo(H_2O)_6^{3+}$:—(a) both reactions are independent of $[H^+] = 0{\cdot}17$—1·0M,[5] (b) the rate constants for the reactions with NCS^- and Cl^- differ and the ratio (*ca.* 60), shows a similar trend to that observed for vanadium(III) (> 37), which has previously been assigned an S_N2 mechanism,[6] (c) rate constants are greater than observed for the ion $Cr(H_2O)_6^{3+}$ (the radius of which is smaller),[7] (d) $\Delta H^{\ddagger}$ values are variable and are significantly less than those for the corresponding reactions of $Cr(H_2O)_6^{3+}$.

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[1] A. R. Bowen and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 3287.

[2] K. Kustin and D. Toppen, *Inorg. Chem.*, 1972, **11**, 2851.

[3] M. Ardon and A. Pernick, *Inorg. Chem.*, in the press (personal communication from Professor Ardon).

[4] T. W. Kallen and J. E. Earley, *Inorg. Chem.*, 1971, **10**, 1152.

[5] For other examples see data for the complexing of thiocyanate to Ti^{3+} (H. Diebler, *Z. phys. Chem.* (*Frankfurt*), 1969, **68**, 64), and V^{3+} (W. Kruse and D. Thusius, *Inorg. Chem.*, 1968, **7**, 464, and B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, 1967, **6**, 1948).

[6] R. C. Patel and H. Diebler, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 1035.

[7] See for example D. Thusius, *Inorg. Chem.*, 1971, **10**, 1106, and references therein.