Spectrophotometric Studies of Complex Formation in Solution between Heptamolybdate(6−) and Manganese(II), Cobalt(II), or Copper(II) Ions

By **Abdul Malik,* Shabbir A. Zubairi,** and **Anjum S. Khan,** Department of Chemistry, University of Karachi, Karachi 32, Pakistan

The reaction between the isopolyanion $[Mo_7O_{24}]^{6-}$ and the bivalent transition-metal ions Mn^{2+}, Co^{2+}, and Cu^{2+} has been studied spectrophotometrically. It is suggested that 1 : 1 complexes are formed in solution. The probable formulation and ligand-field spectra of the 1 : 1 complexes are discussed. The formation constants of the complexes are small, 200—1 000 dm^3 mol^{-1}.

THE isopolyanion [1,2] $[Mo_7O_{24}]^{6-}$ reacts with a number of metal ions (M^{x+}) such as Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Rh^{3+}, Ga^{3+}, and Ni^{2+} to form hexamolybdometallates of the general formula $[MMo_6O_{24}H_6]^{(6-x)-}$ with the Anderson–Evans structure.[3] The chemistry of these anions is well understood.[4,5] When the metal ion is Mn^{2+}, Co^{2+}, or Cu^{2+}, however, the reaction appears to be different in several respects, as indicated by u.v. spectra, spectrophotometric titrations, pH measurements, and the intensity and position of the ligand-field bands. Thus when a solution of Mn^{2+}, Co^{2+}, or Cu^{2+} is mixed with a solution of $[Mo_7O_{24}]^{6-}$ the tail of the charge-transfer (c.t.) band of $[Mo_7O_{24}]^{6-}$ shifts towards longer wavelengths and the ligand-field band of copper and cobalt becomes much more intense. The solution of Mn^{2+}–$[Mo_7O_{24}]^{6-}$ becomes yellow, indicating some interaction. From such solutions, solids have been isolated by Rosenheim *et al.*[6] and La Ginestra *et al.*[7] On the basis of the analysis of these solids, which apparently cannot be recrystallised,[7] it was concluded that Mn, Co, Cu, and Zn also form hexamolybdometallates. *X*-Ray diffractometer traces of the ammonium salts of the anions containing Mn^{2+}, Co^{2+}, and Cu^{2+} synthesised by us according to the method of La Ginestra *et al.* are not identical with those of the ammonium salts of hexamolybdonickelate which is a well established heteropolyanion.[4,5]

We have made a systematic study of solutions containing Cu^{2+}, Co^{2+}, or Mn^{2+} and $[Mo_7O_{24}]^{6-}$ by spectrophotometric titrations and also by the Job method of continuous variation.[8] This paper describes the probable formulation of the complexes formed.

EXPERIMENTAL

Plots of spectrophotometric titrations and various spectra are shown in Figures 1 and 2. The Job and spectrophotometric titrations performed at different experimental conditions were reproducible. Stock solutions of $[Mo_7O_{24}]^{6-}$ were freshly made for each set of measurements by dissolution of AnalaR grade hexa-ammonium heptamolybdate. The maximum change in pH in all the solutions during the spectrophotometric measurements was less than 0.3 unit.

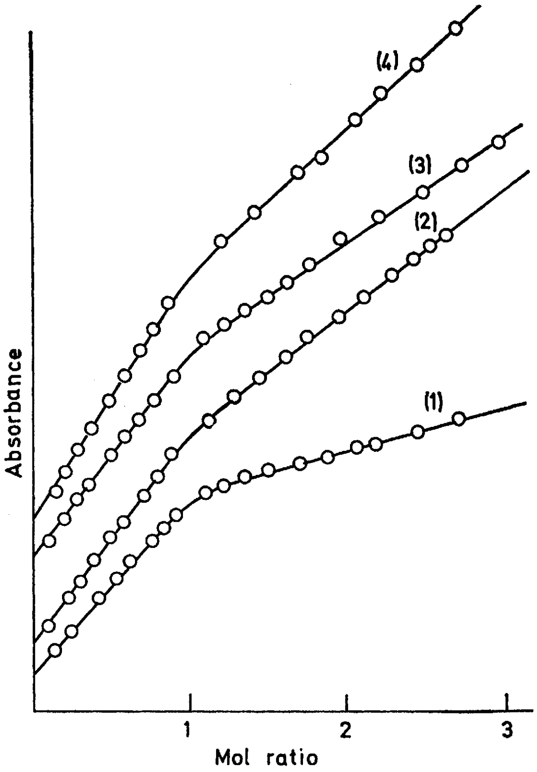

FIGURE 1 Spectrophotometric titrations at 420 nm: (1) and (3), Co^{2+}–$[Mo_7O_{24}]^{6-}$; (2) and (4), Mn^{2+}–$[Mo_7O_{24}]^{6-}$. For (1) and (2), the concentration of $[Mo_7O_{24}]^{6-}$ was constant and that of the metal ion was varied; for (3) and (4), the concentration of the metal ion was constant and that of $[Mo_7O_{24}]^{6-}$ was varied

All the spectrophotometric measurements were made on Unicam SP 500 or SP 800 spectrophotometers.

RESULTS AND DISCUSSION

The Job and spectrophotometric-titration plots suggest that a 1 : 1 complex is formed between $[Mo_7O_{24}]^{6-}$(L)

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and the Mn^{2+}, Co^{2+}, or Cu^{2+} ions (M). There was no evidence for the formation of a 1 : 2 or any other complex even in large excess of M or L. The complex $[ML]^{4-}$ can be regarded as an outer-sphere M,L (ion pair) or as a weak inner-sphere species. We believe that the complex $[M(OH_2)_{6-n}Mo_7O_{24}]^{4-}$ is formed by sharing n oxygen atoms of the heptamolybdate ion.[3,9] A model of $[Mo_7O_{24}]^{6-}$ suggests that there are several ways in which it could co-ordinate to a metal through one, two, three, or even four oxygen atoms. Thus the $[ML]^{4-}$ complex has a distorted MO_6 chromophore. However, whatever the value of n in the complex, the interaction is weak as is evidenced by the ligand-field spectra of M in excess of L. The apparent change in the spectra of cobalt or copper aqua-ions on $[ML]^{4-}$ formation is enhancement of the intensity (*ca.* 3.5 times in the former and 1.5 times in the latter case) and not in the position of the bands, which suggests that the MO_6 chromophore is more distorted than the corresponding aqua-ion. These aqua-ions are expected to have Jahn–Teller distortions.[10] The foregoing discussion rules out an ion-pair model of the complex where a change in the first co-ordination sphere of the metal ion is not expected. Moreover, the enhancement of the intensity of the *d–d* bands has been suggested by several other workers [11] as a distinguishing feature of complex ion pairs. A partial contribution to the intensity enhancement of the band at 20 000 cm^{-1} of cobalt in $[CoL]^{4-}$ because of intensity stealing from the c.t. part of the spectrum cannot be entirely ruled out. However, this is unlikely to be important in the case of $[CuL]^{4-}$ since the ligand-field band is far away from the tail of the c.t. band.

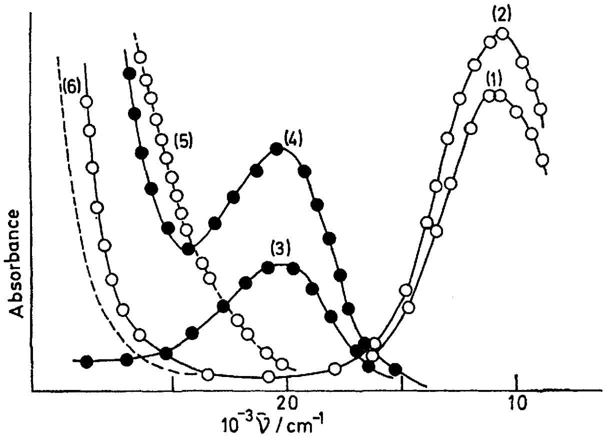

FIGURE 2 Solution spectra: (1) $[Cu(OH_2)_6]^{2+}$; (2) $[Cu(OH_2)_6]^{2+}$ in excess of $[Mo_7O_{24}]^{6-}$ (L); (3) $[Co(OH_2)_6]^{2+}$; (4) $[Co(OH_2)_6]^{2+}$ in excess of L; (5) $[Mn(OH_2)_6]^{2+}$ in excess of L; and (6) L. The absorbance in (1) and (3) has been exaggerated to clarify the comparison with (2) and (4)

That the ligand in the $[ML]^{4-}$ complex is intact and is not degraded to form hexamolybdometallate is suggested by the following considerations. Spectrophotometric titrations performed under widely different experimental conditions indicate that the end-point is at a M : Mo ratio of 1 : 7, not at 1 : 6. The u.v. spectrum (25 000—50 000 cm^{-1}) of a solution of ligand, at three different concentrations, in a large excess of metal, overlapped the spectrum of a solution containing the same concentration of the ligand, indicating that the ligand is intact. A similar experiment where M = Cr^{3+} gave the spectrum of hexamolybdochromate(III). Further support for the formulation suggested here is given by the ligand-field spectra of Cr^{3+}, Co^{3+}, and Ni^{2+} in hexamolybdometallates where the metal ions are in the centre [3] of the complex $[MMo_6O_{24}H_6]^{(6-x)-}$. In all these complexes the ligand-field experienced by the metal ion is larger, and the intensity of the *d–d* transitions is smaller than (or comparable to), that in the corresponding aqua-ions.[4,5] The above pattern of ligand-field strength and intensity of the bands, which is contrary to our observations, is also expected if the $[ML]^{4-}$ complexes are actually hexamolybdometallates.

Additional support for the suggested formulation comes from the pH measurements. In all the titrations the maximum pH change was less than 0.3 unit and it is unlikely that such a small change in pH would accompany degradation of L. In the system Cr^{3+}–$[Mo_7O_{24}]^{6-}$, where it is known that the $[Mo_7O_{24}]^{6-}$ ion degrades, the pH change is more than 2.5 units. The formation constants (K) of the $[ML]^{4-}$ complexes calculated by the method of Reilley and Sawyer [12] are small, 2×10^2—10^3 dm^3 mol^{-1}, compared with the reported log K values of $[NiMo_6O_{24}H_6]^{4-}$ and $[CrMo_6O_{24}H_6]^{3-}$ which are *ca.* 31 and *ca.* 55 respectively.[4,13]

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