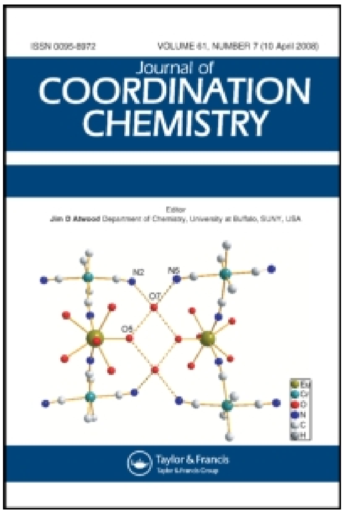

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THE AQUEOUS EQUILIBRIA OF CHROMIUM(II) WITH FORMATE ION. EVIDENCE FOR A WEAK CHROMIUM-CHROMIUM MULTIPLE BOND

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The equilibria of Cr(II) with formate ion in aqueous media have been analyzed by spectrophotometric and nuclear magnetic resonance techniques. A binuclear complex is observed to be incompletely formed throughout the intermediate formate ion concentration range and is suggested to be structually analogous to the quadruply metal–metal bonded dichromium tetraacetate. This complex is formed via the equilibrium

$$2\ \mathrm{Cr(Formate)}^{+} + \mathrm{Formate}^{-} \rightleftharpoons \mathrm{Cr}_2(\mathrm{Formate})_3^{+}$$

for which the equilibrium constant is $2.1 \pm 0.2\ \mathrm{M}^{-2}$. At the highest formate ion concentrations studied, the binuclear complex dissociates to mononuclear high-spin complexes with formate to metal ion ratios greater than 3. The existence of the binuclear complex in only a narrow ligand concentration range suggests that the chromium–chromium bond is of marginal importance to the stability of the binuclear species and is subordinate to chromium(II)-formate ion bond strength.

INTRODUCTION

There has been considerable recent interest in the study of binuclear complexes of d^4 metal ions containing a quadruple metal–metal bond.[1] Much of the work has dealt with complexes of Re(III) and Mo(II) because the bond has been suggested to be extraordinarily strong in these compounds.[2] Certain Cr(II) complexes contain Cr-Cr quadruple bonds but these are generally, though not exclusively, complexes with bridging ligands. The large number of mononuclear Cr(II) complexes suggests that the Cr-Cr quadruple bond may be rather weak. However, the exceptional shortness of the bond in several complexes is suggestive of considerable strength.[3,4]

Carboxylic acids react with chromium(II) to form binuclear complexes which are red and nearly diamagnetic.[5] The diamagnetism and short Cr-Cr bond in the acetate suggest that the bond is of order 4.[6] Other alkyl corboxylates are known and their similar red color, magnetic properties, and stoichiometries suggest that they too contain Cr-Cr quadruple bonds. Chromous formate differs significantly from these complexes. Several forms of the compound have been crystallized from aqueous solution and it has been hypothesized that some are mononuclear and others binuclear.[7] A red, nearly diamagnetic form has been isolated and it is converted to a blue, highly paramagnetic form upon heating, suggestive of a binuclear quadruply bonded species being converted to mononuclear forms.[8] In order to learn more about the factors leading to stabilization of the binuclear form of this compound, we have carried out spectroscopic study of the chromous ion–formate ion aqueous system under equilibrium conditions.

EXPERIMENTAL

Chromous ion solutions were prepared by reduction of an aqueous 1M chromic chloride solution of zinc amalgam. To remove zinc(II), chromous formate was prepared by adding solid sodium formate to a 1M chromous chloride solution under nitrogen until the total formate ion concentration was 5M. Upon standing, red chromous formate precipitated. It was washed with small portions of mother liquor, followed by absolute ethanol or acetone. Solutions for equilibria and magnetic studies were prepared from this chromous formate. All solutions were 1.15M in formic acid to avoid autoxidation. Appropriate amounts of sodium formate were added and aliquots were taken for the visible spectroscopic and nuclear magnetic resonance measurement using "airlessware" and standard anerobic techniques.[9] All data discussed

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herein were taken on systems with formate ion concentrations greater than twice the Cr(II) concentration. Under these conditions negligible formate bonding occurs through interaction of Cr(II) with formic acid which was demonstrated by pH measurements.

Visible spectra were obtained on a Cary 14 and nmr spectra were recorded on a Perkin Elmer R24-A. In the nmr experiments, tris(ethylenediamine)-chromium(III) chloride was used to calibrate the solvent shift due to paramagnetic susceptibility. In the evaluation of equilibrium constants from visible spectra, measurements of absorbance were made at 600 nm where the binuclear complex absorbs strongly and the mononuclear forms absorb relatively weakly calculations were checked for consistency with values determined at 500 and 550 nm. The extinction coefficient for the binuclear form was determined by difference from solutions with low formate concentration and the value of 79 was confirmed by increasing the alcohol content of the solution to 50%, under which conditions the binuclear complex is completely formed. Further increases in alcohol content did not change the absorption spectrum significantly. The concentrations of mononuclear and binuclear complexes were calculated from the observed absorption. The various equilibrium models were tested by calculating the equilibrium constant assuming each model for all data. As it turned out only one model led to a calculated equilibrium constant which did not depend monotonically on the concentration of one of the components of the system (*vide infra*). More elegant methods of data reduction were therefore deemed unnecessary. The temperature was controlled at 25°C during these measurements. No significant oxidation was observed during the measurements on either instrument. All spectral changes brought about by increasing concentration were fully reversible upon dilution. It is important to recognize that at the high concentrations of reagents necessarily employed to observe the equilibria all solutions are expected to be significantly non-ideal. Under these conditions, ionic strength cannot be held constant and it is impractical to apply activity corrections. Therefore the equilibrium constants reports can only be considered estimates of the true thermodynamic values.

RESULTS

As the formate ion concentration is varied at constant Cr(II) concentration relatively complex changes are observed in the visible region of the absorption spectrum. As Figure 1 illustrates, these changes involve the formation of a broad band at 500 nm at intermediate formate ion concentration and its subsequent loss at high formate ion concentration to give a band at 615 nm. Visually this corresponds to the formation of a red complex which can be converted to a blue-violet species, by addition of further formate ion. These changes are dependent on the total concentration of Cr(II). The 500 nm band is clearly visible if the Cr(II) concentration is 0.05 M or above while at 0.01 M and below, it cannot be resolved at any formate ion concentration. In aqueous solution the species giving rise to the 500 nm band is never completely formed. Addition of ethanol stabilizes it until at 50 mole percent aqueous ethanol the red complex is formed to the exclusion of either the initial mononuclear aqueous Cr(II) complex or the final blue violet species.

At low formate ion concentration the species giving rise to the 615 nm band is not formed significantly. Under these conditions, the stoichiometry of the species giving rise to 500 nm band may be easily investigated by analyzing the spectral changes accompanying the variation of the concentrations of Cr(II) and of formate ion. The degree of formation of this complex depends linearly on the formate ion concentration and on the square of the Cr(II) ion concentration. Such behavior can be accounted for in a simple way only by the equilibrium expressed in equation 1. In order to determine

$$\mathrm{Cr(Formate)}_x^{2-x} + \mathrm{Cr(Formate)}_y^{2-y} + \mathrm{Formate}^- \rightleftarrows \mathrm{Cr_2(Formate)}_{x+y+1}^{3-x-y} \quad 1.$$

the values of x and y, values of the equilibrium constant K were calculated from the concentrations of the various species determined spectrophotometrically using all combinations of x and y from 0 to 4. These trial constants were calculated for fifteen different concentrations of formate ion and Cr(II). Only for x=y=1 were values of K determined that were independent of both the concentration of Cr(II) and of formate ion. Table 1 lists representative values of the calculated equilibrium constant at different concentrations of the reactants using this equilibrium model. Other values of x and y lead to calculated values of K which depend monotonically on the concentrations.

Mononuclear Cr(II) complexes have magnetic moments corresponding to 2 or 4 unpaired electrons while the binuclear $\mathrm{Cr_2^{+4}}$ complexes are diamagnetic, or nearly so. Therefore an independent means of probing the equilibrium of Cr(II) with formate ion is to study the chemical shift and linewidth of the proton resonance of water as Cr(II) and formate ion concen-

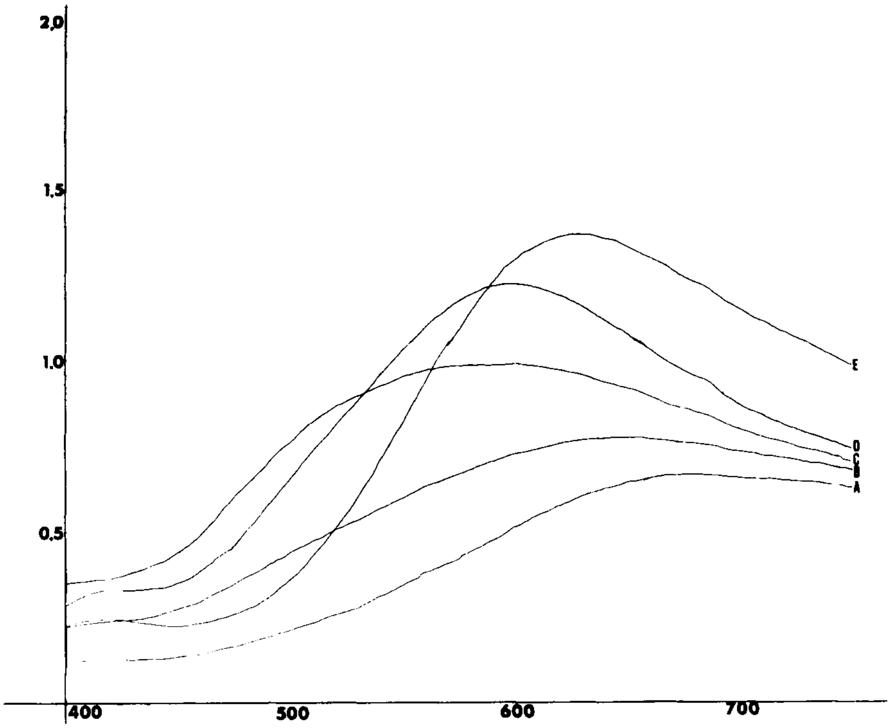

FIGURE 1 Changes in the absorption spectrum of chromous ion during the addition of sodium formate. All solutions are 1.15 M in formic acid and the Cr(II) concentration is 0.10 M. In curve A formate = 0.2 M, B = 0.4 M, C = 0.8 M, D = 2.2 M, E = 6.2 M.

TABLE I

Calculated values of the equilibrium constant for formation of binuclear chromous Formate using the formation expression in Eq. (1) with x = 1, y = 1.

Total Cr(II)	Total Formate Ion	K
0.20 M	0.40 M	2.0
0.16	0.40	2.1
0.12	0.40	2.0
0.10	0.20	3.2
0.10	0.20	3.0
0.10	0.40	2.4
0.10	0.50	2.1
0.10	0.80	1.7
0.10	0.80	2.0
0.10	1.0	1.7
0.10	1.1	1.9
0.08	0.4	3.2
0.05	0.1	2.9
0.05	0.2	2.4
0.05	0.3	2.4
0.05	0.4	2.8
0.05	0.5	2.7
0.05	0.6	2.5
0.05	0.7	2.1
0.05	0.8	2.0
0.05	0.9	2.1
0.05	1.0	2.0

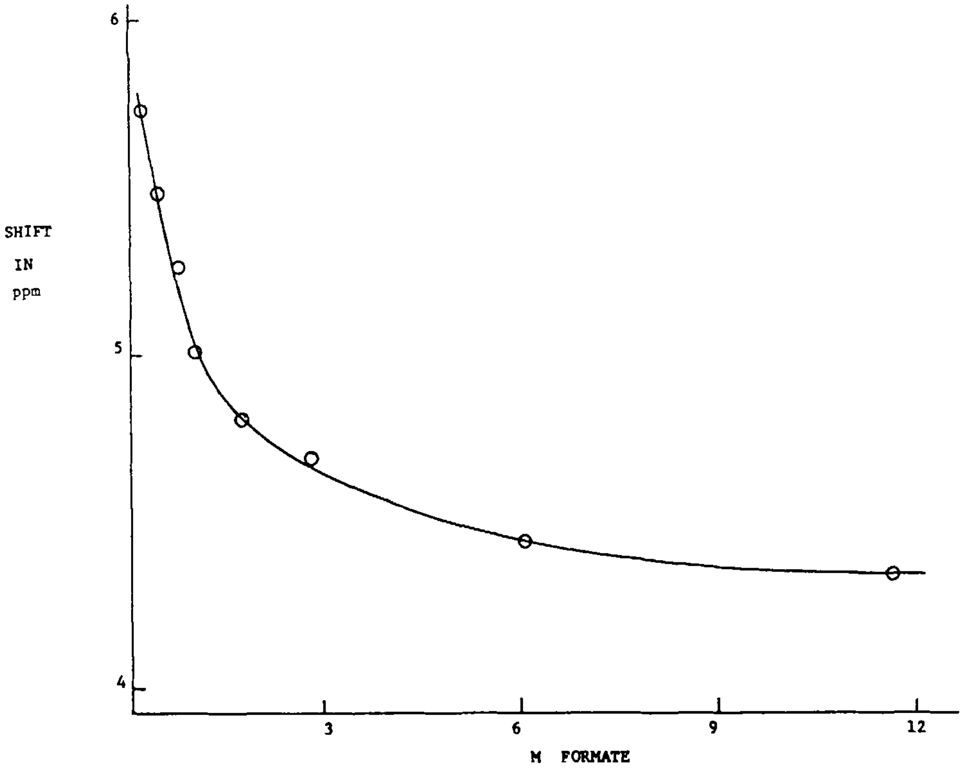

FIGURE 2 Changes in the proton magnetic resonance chemical shift of water as formate ion concentration is varied in a solution 1.15 M in formic acid and 0.5 M in total Cr(II). In the absence of Cr(II) the chemical shift of water is 4.8 ppm. The water resonance is calculated to appear at 4.19 ppm when it experiences a bulk paramagnetic shift from a 0.5 M concentration of four unpaired electron spins. Tetramethylsilane was used as an external reference.

trations are varied. Figure 2 presents representative data on the dependence of chemical shift on formate ion concentration while Figure 3 plots the linewidth of the water resonance for the same experiments. The water resonance is influenced by a number of factors; however four important observations can be made.

a) In the absence of added formate ion, the water resonance is shifted to lower field from its position in pure water. This is opposite to the shift resulting from the bulk paramagnetism and therefore reflects the rapid averaging of the chemical shift of coordinated water with that of the uncoordinated solvent.

b) At low concentration of formate ion, both the linewidth and frequency of the water resonance are linearly dependent on formate ion, in accord with Eq. 1.

c) The minimum of the linewidth in Figure 3 corresponds to maximum formation of the complex giving rise to the 500 nm absorption in the visible spectrum. This is consistent with a reduced, or possibly zero, paramagnetic moment for this species.

d) At the highest formate concentration the water resonance moves to high field from its diamagnetic position and approaches the value expected if the shift is due only to the bulk paramagnetism of a Cr(II) complex having 4 unpaired electrons and no coordinated water.

DISCUSSION

In the aqueous Cr(II) formate system it is apparent that increasing formate concentration causes the formation of a red binuclear complex. The square dependence of the degree of formation of the red species on mononuclear Cr(II) concentration is clear evidence that the red complex is binuclear. These equilibria data also reveal a linear dependence of the formation of the binuclear complex upon formate ion concentration, indicating that the binuclear complex forms with the stepwise addition of a simple formate ion to a pair of mononuclear Cr(II) complexes. Other

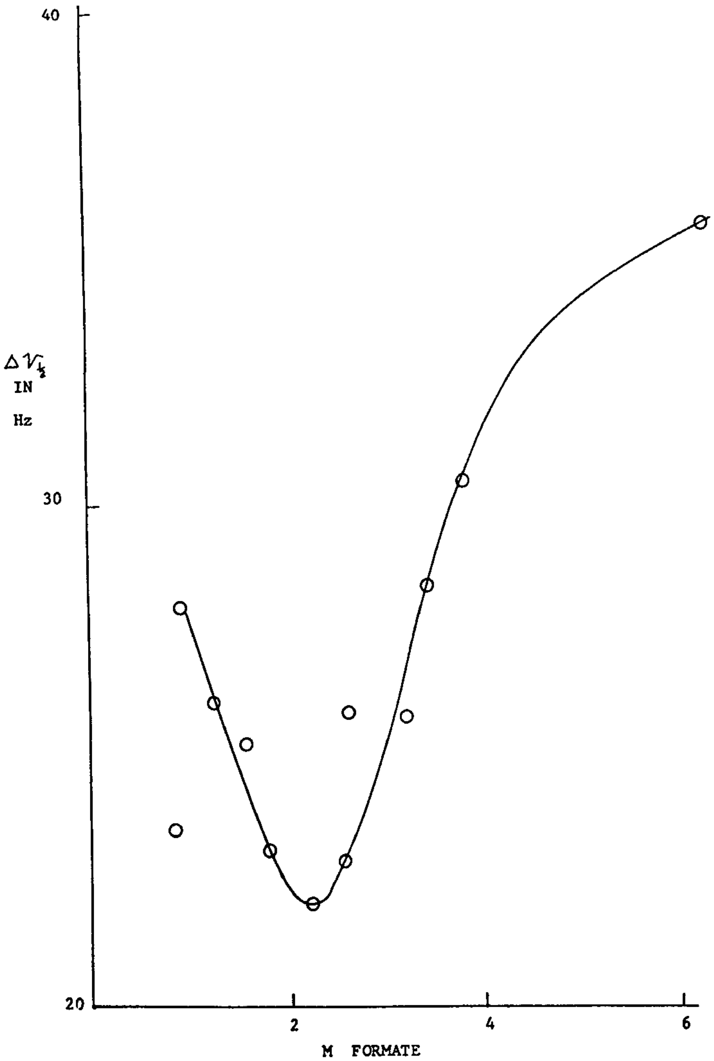

FIGURE 3 Dependence of the proton magnetic resonance linewidth of water as formate ion concentration is varied in a solution 1.15 M in formic acid. The linewidth is full width at half-maximum height. The total Cr(II) concentration is 0.5 M for all points.

features of the equilibrium are less clear. Although equation with x = 1, y = 1 gives a calculated equilibrium constant which is independent of concentrations for our data, it must be kept firmly in mind that at the high concentrations under which this work was necessarily carried out, ionic strength cannot be controlled and the solutions are expected to be significantly non-ideal. Regardless of which of the combinations of x and y is the correct one, the units of the reported equilibrium constant remain the same, and the magnitude very nearly the same.

At higher still formate ion concentrations the red binuclear complex reverts to a blue paramagnetic species. This complex has a single broad absolution at 615 nm characteristic of mononuclear high-spin Cr(II) complexes. A determination of the stoichiometry of the product from equilibrium data could not be trusted because of the very high formate ion concentration required. However, the magnetic and absorption spectral data are consistent with a mononuclear high-spin Cr(II) complex with at least four formate ligands. In Figure 2 at the highest formate ion concentration, the solvent shift approaches but does not reach the value expected for bulk paramagnetic susceptibility shifting due to a complex with 4 unpaired electrons. Since a downfield shift is observed for coordinated water at low formate ion concentration, failure of the water peak to reach the point anticipated for four unpaired electrons at high formate concentration could be due to the observed position being a combination of the upfield shift due to bulk paramagnetism averaged with a downfield shift due to chemical exchange with one or two bound water molecules in the product complex.

Tetraacetatodichromium(II) has been most thoroughly studied of the binuclear Cr(II) carboxylates.[10,11,12] Like the formate system reported on herein a monomer-dimer equilibrium is observed but it is independent of acetate ion concentration and has the form of equation 2. Unlike the formate case described herein,

$$2\ \mathrm{Cr(Acetate)}_n \rightleftharpoons \mathrm{Cr_2(Acetate)}_{2n} \qquad (2)$$

no dissociation of the dimer via addition of further acetate is reported at high acetate concentration. The qualitative difference between the acetate and formate complexes evidently reflects a significant difference between the abilities of the two ligands to stabilize the quadruple bonded binuclear complex. This is surprising in view of the similarity of the two ligands. The difference between these ligands is also manifested in the absorption spectra of the binuclear complexes. The acetate has a visible absorption maximum at 460 nm while we report the formate maximum to be at 500 nm.

A final point of discussion concerns the strengths of the multiple chromium–chromium bond. The equilibria data indicate that three formate ions in the bridging bidentate mode are required to stabilize the multiple bonded complex. Yet at the highest formate concentrations the multiple metal–metal bond is not sufficiently strong to hold the complex together. It dissociates into mononuclear species with the loss of that bond and with the conversion of the bonding of the formate ligands from bridging bidentate to simple monodentate coordination. Ignoring solvation energies the dissociation of the binuclear complex at high formate ion concentrations implies that the quadruple bond cannot be stronger than a small integral multiple of the difference between bridging bidentate and monodentate formate to Cr(II) bond energies. We infer that the dichromium carboxylates owe their stability in large part to the bridging carboxylate ligand and to a significant but lesser degree to the quadruple bond.

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REFERENCES

1. F. A. Cotton, Centenary Lecture, *Chemical Society Reviews*, 4, 27 (1975).
2. F. A. Cotton, *Accounts Chem. Res.*, 2, 240 (1969).

3a. G. Albrect and D. Stock, *Z. Chem.*, 7, 321 (1967).

3b. T. Aoki *et al. Bull. Chem. Soc. Japan*, **42**, 545 (1969).

4. J. Krause and G. Schodl., *J. Organomet. Chem.*, 27, 59 (1971).
5. S. Herzog and W. Kalies, *Z. Anor. Chem.*, **329**, 83 (1964).
6. F. A. Cotton *et al.*, *J. Amer. Chem. Soc.*, **92**, 2926 (1970).
7. S. Herzog and W. Kalies, *Z. Chem.*, **4**, 183 (1964), **5**, 273 (1965), **6**, 344 (1966), *Z. Anorg. Chem.*, **351**, 237 (1967).
8. A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *Proc. Chem. Soc.*, 281 (1963)
9. D. F. Shriver, *The Manipulation of Air-Sensitive Compounds*, McGraw-Hill Inc., New York, N.Y. (1969).
10. R. D. Cannon, *J. Chem. Soc.*, A 1098 (1968).
11. R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, **14**, 2202 (1975).
12. R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, **14**, 2207 (1975).