Equilibria between Di-Hydroxo- and Hydroxo-bridged Dimers of Chromium(III)

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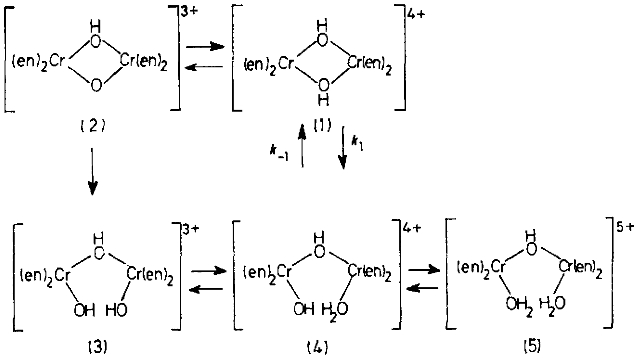
Summary The new dimers (**2**), (**3**), and (**4**) have been isolated as salts and the equilibrium between (**1**) and (**4**) has been shown to be established within minutes in aqueous solution.

Current interest in the chemistry of hydroxo-bridged dimers of metal ions prompts this report on the reversible ring-opening and ring-closure of the cation (**1**), and on the isolation of the single bridged dimers (**3**) and (**4**) as salts. The dimeric structure of (**1**), which was originally proposed by Pfeiffer,[1] has now been established by an *X*-ray structure analysis[2] of $[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_2Cl_2, 2H_2O$. The isomer investigated is shown to be the *meso*-isomer.

The dimer (**1**) shows acidic properties due to the hydroxo-bridges as reported for the 1,10-phenanthroline and 2,2'-bipyridine Cr^{III} analogues.[3,4] Dissolution of the perchlorate of (**1**) in NaOH instantaneously yielded a blue solution of (**2**) which was isolated as a blue-green perchlorate salt. By addition of $HClO_4$ to a solution of (**2**) or to its perchlorate salt (**1**) reformed instantaneously. The acid dissociation constant of (**1**) was spectrophotometrically estimated in water (p$K \simeq 12$, 20 °C). The much lower acid dissociation constants reported for the 1,10-phenanthroline and 2,2'-bipyridine dimers (p$K \simeq 7{\cdot}5$, 1 M $NaNO_3$) are in accordance with the π-acid character of the aromatic ligands.

At room temperature the blue solution of (**2**) changed within a few minutes to reddish-purple owing to the formation of (**3**). It is not known whether the formation of (**3**) in basic solution proceeds *via* (**2**) (see Figure), or *via* (**1**) and (**4**). When $HClO_4$ was added to a solution of (**3**), the colour shifted instantaneously towards red as (**4**) was formed. Both (**3**) and (**4**) were isolated as red perchlorate salts.



The lower limit of the first acid dissociation constant of (**5**), K_1, was estimated spectrophotometrically and potentiometrically as $pK_1 \leqslant 1$ (1 M $NaClO_4$, 0 °C). The second acid dissociation constant of (**5**), K_2, was determined potentiometrically as $pK_2 = 7{\cdot}95$ (1 M $NaClO_4$, 0 °C). The visible absorption spectra (0 °C) of the perchlorate salt of (**4**) in 1 M $NaClO_4$ (pH 5) and in 5 × 10^{-3} M $HClO_4$–1 M $NaClO_4$ were identical, while in 1 M $HClO_4$, a blue-shift of the first absorption band, due to partial protonation of (**4**) to give (**5**), was observed. Thus, (**5**) is a much stronger acid than the analogous compound acid erythro-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]^{5+}$ ($pK = 2{\cdot}8$, 0·14 M $NaClO_4$).[5] The low pK_1 of (**5**) explains to some extent the observation[6] that the rate of acid hydrolysis of (**1**) to form the monomeric cation *cis*-$[Cr(en)_2(H_2O)_2]^{3+}$ is independent of $[H^+]$ for acid concentrations between 0·2 and 1·0 M. The pK_2 of (**5**) is comparable with that reported for the monomeric cation *cis*-$[Cr(en)_2(OH)(H_2O)]^{2+}$ ($pK_2 = 7{\cdot}17$, 1 M $NaNO_3$, 25 °C).[7]

We did not observe deprotonation of (**3**) to the corresponding μ-oxo dimer in strong base (up to 1 M NaOH). This corresponds to the observation that the compound basic erythro-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]^{4+}$, does not deprotonate even in strong NaOH.[5]

In accordance with the dimeric structure proposed for (**3**) and (**4**), these could be transformed back into (**1**). Aqueous solutions of (**4**), obtained by dissolving either the perchlorate salt of (**4**) in water, or the perchlorate salt of (**3**) in perchloric acid, yielded (5 min, 20 °C), an equilibrium mixture of (**1**) and (**4**), from which the less soluble perchlorate salt of (**1**) was isolated by addition of $NaClO_4$. The solid perchlorate salt of (**4**) yielded that of (**1**) by heating (10 min, 60 °C). The observed blue-shift of the first absorption band of (**4**) (λ_{max} 516 nm) relative to that of (**3**) (λ_{max} 526·5 nm) follows the spectrochemical series. (**1**) has a corresponding band (λ_{max} 540 nm), as has the 1,10-phenanthroline analogue (λ_{max} 541 nm).[4]

The spectra of solutions (1 M $NaClO_4$, 0 °C) of the perchlorate salts of (**1**) and (**4**) changed rapidly, upon dissolution, but after 90 min became identical and almost constant. In both cases a well defined isosbestic point (ϵ, 169 l mol^{-1} cm^{-1}, λ 512 nm) was observed. From the spectrophotometric measurements the equilibrium constant $K = [(\mathbf{4})]/[(\mathbf{1})]$ was 0·83 (1 M $NaClO_4$, 0 °C). First-order plots of $\log(OD_t - OD_\infty)$ against time were linear to *ca.* 90% completion, and from the gradients ($k_{obs}/2{\cdot}303$) values of the rate constants, k_{obs}, were calculated. k_{obs} values obtained from measurements on solutions initially composed of either (**1**) or (**4**) were identical and were independent, to 0·046 min^{-1}, of $[H^+]$ over the range investigated, 5 × 10^{-3} M $HClO_4$, 1 M $NaClO_4$–1 M $NaClO_4$ (pH 5), at 0 °C. The rate constants were then calculated to $k_1 = 0{\cdot}021\ min^{-1}$ and $k_{-1} = 0{\cdot}025\ min^{-1}$.

At room temperature, $k_{obs} \simeq 0{\cdot}6\ min^{-1}$ (20 °C, pure water), which means that earlier reported measurements on the diol in aqueous solution probably refer to the equilibrium mixture.[6] These rate constants are unusually large compared with analogous reactions of Cr^{III} involving Cr–O bond rupture. Thus, k_{-1} is several orders of magnitude greater than the rate constant for water exchange in $[Cr(H_2O)_6]^{3+}$.[8]

An analogous equilibrium between mono-ol and diol has been reported for the cations $[(H_2O)_4Cr(OH)_2Cr(OH_2)_4]^{4+}$ and $[(H_2O)_5Cr(OH)Cr(OH_2)_5]^{5+}$.[9]

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