

Synthesis and Characterization of a Phosphato-Bridged Binuclear Chromium(III) Complex

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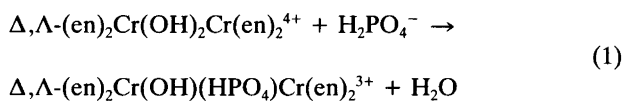
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The reactions of the dinuclear complex $\Delta, \Lambda\text{-(en)}_2\text{Cr(OH)}_2\text{-Cr(en)}_2^{4+}$ with anions of organic and inorganic acids have been shown to give hetero-bridged species of the type $\Delta, \Lambda\text{-(en)}_2\text{Cr(OH)(X)Cr(en)}_2^{2+}$ [$X = \text{SO}_4^{2-}$, HCOO^- , CH_3COO^- , CF_3COO^- and $\text{RCH(NH}_2\text{)COO}^-$] or singly bridged species of the type $\Delta, \Lambda\text{-X(en)}_2\text{Cr(OH)Cr(en)}_2\text{Y}^{2+}$ ($X = \text{Cl}^-$, $Y = \text{H}_2\text{O}$ or $X = Y = \text{Cl}^-$ or $X = \text{CF}_3\text{COO}^-$, $Y = \text{H}_2\text{O}$).¹⁻⁷ Two of the dibridged species have been characterized by X-ray crystal-structure analysis ($X = \text{SO}_4^{2-}$ and CF_3COO^-).^{3,7} Studies of this type of complex are of relevance to biological systems, since many metallo-enzymes contain binuclear metal complexes as the active site, and very often the two metal ions are bound together with two (or three) bridges of the kind mentioned above. In continuation of our previous studies of this type of complex we have initiated an investigation of the reactions of phosphate with binuclear complexes, and report the synthesis of the dibridged complex $\Delta, \Lambda\text{-(en)}_2\text{Cr(OH)(HPO}_4\text{)Cr(en)}_2^{3+}$. This complex has relevance to the study of model systems for the metal-ion catalyzed metabolism of phosphate, which is believed to involve a binuclear metal complex (usually containing Mn, Zn or Cu) at the active site.⁸⁻¹¹

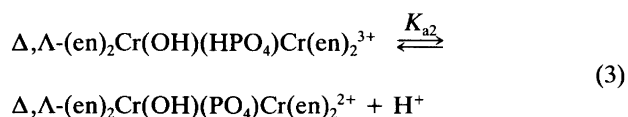
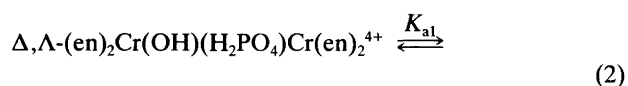
Results and discussion

In the present study the complex $\Delta, \Lambda\text{-[(en)}_2\text{Cr(OH)}_2\text{-Cr(en)}_2\text{]ClO}_4$ was shown to react with phosphate at pH 2 as shown in eqn. (1). The reaction is relatively slow ($t_{1/2} = 1/2$ h in 0.1 M H_3PO_4 , 0.2 M NaH_2PO_4 at 25 °C) and quantitative, shown spectrophotometrically.



The complex was isolated as a perchlorate salt (yield 76 %). The phosphato-bridged species is very stable in acidic, neutral and weakly basic media, i.e. at 25 °C the absorption spectra do not change significantly within the first 20 min. In strong base a slow reaction was observed ($t_{1/2} \approx 1$ h in 1 M NaOH), but the reaction was not further studied.

The change of the spectra of aqueous solutions of $\Delta, \Lambda\text{-[(en)}_2\text{Cr(OH)(HPO}_4\text{)Cr(en)}_2\text{]ClO}_4 \cdot \text{H}_2\text{O}$ with pH (0–14) could be interpreted unambiguously in terms of two acid–base equilibria, as shown in eqns. (2) and (3).



The concentration acid dissociation constant of the dihydrogenphosphato bridge, $\text{p}K_{a1}$, was determined from the spectra of $\Delta, \Lambda\text{-[(en)}_2\text{Cr(OH)(HPO}_4\text{)Cr(en)}_2\text{]ClO}_4 \cdot \text{H}_2\text{O}$ in solutions with $[\text{H}^+] = 10^{-5} - 1.0$ M in 1 M (Na,H)Cl at 25 °C, as illustrated in Fig. 1 for one wavelength. Using the change of the absorbance for 301 different wavelengths in the region 300–600 nm, this gave the value $\text{p}K_{a1} = 1.582(2)$. The concentration acid dissociation constant of the hydrogenphosphato bridge, $\text{p}K_{a2}$, was determined from a potentiometric titration of $\Delta, \Lambda\text{-[(en)}_2\text{Cr(OH)(HPO}_4\text{)Cr(en)}_2\text{]ClO}_4 \cdot \text{H}_2\text{O}$ with base, which at 25 °C gave $\text{p}K_{a2} = 6.192(3)$ in 1 M Na(Cl,OH). In agreement with the spectroscopic measurements, the titration showed that no other acid–base reaction occurs for pH up to ca. 11. Spectral data for the three species are given in Table 1.

Note that the above results are in agreement with the proposed structure. The notion that the isolated complex

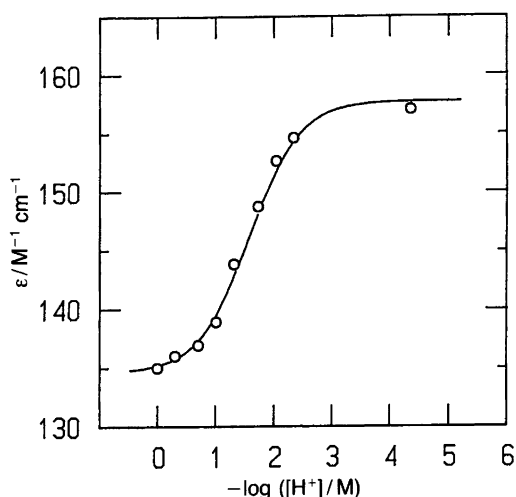


Fig. 1. Change of the absorbance with $[H^+]$ for solutions of Δ, Λ - $[(en)_2Cr(OH)(HPO_4)Cr(en)_2](ClO_4)_3 \cdot H_2O$ in 1 M (Na,H)Cl at 25 °C measured at $\lambda = 550$ nm. The solid line has been calculated using $pK_{a1} = 1.582$.

could be a monohydroxo-bridged species, Δ, Λ - $[(H_2O)(en)_2Cr(OH)Cr(en)_2(HPO_4)](ClO_4)_3$, can be rejected, since in that case two acid dissociation constants would have been observed during the titration with base. Also, it is noted that the reactions of aqueous solutions of Δ, Λ - $[(en)_2Cr(OH)(HPO_4)Cr(en)_2](ClO_4)_3 \cdot H_2O$ with acid or base occur very rapidly ($t_{1/2}$ is estimated to be less than 1 s at 0 °C), as expected for acid–base reactions, and it is therefore certain that any reactions involving Cr–O–(phosphate) bond breaking can be excluded.

In Table 2 the acid dissociation constants for the phosphato bridge are compared with the values for an analogous dibridged cobalt(III) species and some selected mononuclear species. First it is seen that monodentate coordination of $H_{3-z}PO_4^{z-}$ to one metal center lowers the pK_a by 2–4 units, and that the effect increases with decreasing z . The effect is larger for bidentate coordination, and this is significantly more pronounced in the mononuclear complex $Co(en)_2HPO_4^{2+}$ (pK_a decreases by 6–8) than in the dinuclear complexes (pK_a decreases by 4–6). This is opposite to the effect expected on the basis of charge considerations. The pK_a values for the present complex are nearly identical with those reported for dibridged cobalt(III) species containing an amido bridge.

It follows from the spectral measurements that even in 1 M NaOH there is no significant deprotonation of the

hydroxo bridge, and pK_a is therefore greater than 14. The hydroxo bridge in the present complex is therefore a much weaker acid than the hydroxo bridge in Δ, Λ - $(en)_2Cr(OH)(SO_4)Cr(en)_2^{3+}$, which has $pK_a = 12$,² and this may at least to some extent be explained by the different charges of the two species.

From the acid–base and spectral properties discussed above it is unambiguously concluded that the proposed phosphato-bridged structure is retained in aqueous solution for the entire pH range (0–14) studied. In this respect the present species behaves similarly to its sulfato-bridged analogue and to a series of carboxylato-bridged chromium(III) species.^{2,5} In contrast, it was recently shown that the corresponding trifluoroacetato complex equilibrates very rapidly with the monohydroxo-bridged species, Δ, Λ - $(H_2O)(en)_2Cr(OH)Cr(en)_2(OCOCF_3)^{4+}$ ($t_{1/2} = 36$ s at 25 °C).⁴

Experimental

Materials and instrumentation. Δ, Λ - $[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ was prepared as described previously.^{18,19} All other chemicals were of analytical grade. Spectra were recorded using a Perkin-Elmer Lambda diode array spectrophotometer. Potentiometric measurements were made with a Radiometer PHM 52 potentiometer using a GK 2301 C combined glass and calomel electrode. The calomel electrode was modified to contain 1 M NaCl.

Measurements and calculations. H, N, C and Cl analyses were performed by the Microanalytical Laboratory of the H. C. Ørsted Institute. The methods for potentiometric and spectrophotometric determinations of the concentration acid dissociation constants have been described previously.²⁰

Synthesis of Δ, Λ - $[(en)_2Cr(OH)(HPO_4)Cr(en)_2](ClO_4)_3 \cdot H_2O$. A solution of Δ, Λ - $[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ (4.0 g, 5.15 mmol) in 0.5 M H_3PO_4 , 1.0 M NaH_2PO_4 (50 ml) was kept at 25 °C for 5 h. During this time the colour of the solution changed from purple to red. A saturated aqueous solution of $NaClO_4$ (20 ml) was then added, and red crystals precipitated within minutes. The product was filtered off and washed with 96 % ethanol and then with diethylether, and was then dried in the air. Yield 3.00 g (75 %). To a filtered solution of the crude product (1.0 g) in water (50 ml, 25 °C) was added a saturated aqueous solution of $NaClO_4$ (20 ml). After 15 min the precipitate was isolated as above. Yield 0.87 g (87 %). The

Table 1. Spectral data for aqueous solutions of Δ, Λ - $[(en)_2Cr(OH)(HPO_4)Cr(en)_2](ClO_4)_3 \cdot H_2O$ as a function of pH at 25 °C.

Complex ion	Solvent	$(\epsilon, \lambda)_{max}$
Δ, Λ - $(en)_2Cr(OH)(H_2PO_4)Cr(en)_2^{4+}$	4 M HCl	(205,514) ^a (119,383) ^a
Δ, Λ - $(en)_2Cr(OH)(HPO_4)Cr(en)_2^{3+}$	0.005 M HCl	(207,519) ^b (126,383) ^b
Δ, Λ - $(en)_2Cr(OH)(PO_4)Cr(en)_2^{2+}$	1 M NH_4Cl , 1 M NH_3	(203,527) ^c (123,383) ^c

^{a-c}Nearly the same values were obtained in 1 M HCl (a), in pure water (b) and in 0.01 M NaOH or 1.0 M NaOH (c).

Table 2. Acid dissociation constants at 25 °C and $I = 1.0$ M.

Acid ^a	$pK_a(H_{3-2}PO_4^{2-})$			$pK_a(H_2O)$	Ref.
	X = H ₃ PO ₄	X = H ₂ PO ₄ ⁻	X = HPO ₄ ²⁻		
X	1.72	5.92	12.3		12,13
Cr(NH ₃) ₅ X		3.0 ^b	7.8 ^b		14
Co(NH ₃) ₅ X	-0.67 ^c	3.6	8.5		13
<i>Cis</i> -Co(NH ₃) ₄ (H ₂ O)X	-0.2 ^d	3.2 ^d	9.2 ^d	6.7 ^d	15
(NH ₄) ₄ Co(NH ₂)(X)Co(NH ₃) ₄		1.5 ^e	6.0 ^h		17
Δ, Λ -(en) ₂ Cr(OH)(X)Cr(en) ₂		1.55	6.17		This work
<i>cis</i> -Co(en) ₂ X		0.0 ^e	4.25 ^f		16

^aCharges omitted. ^b17.1 °C. ^c $I = 3$ M. ^d5.0 °C. ^e10 °C and $I = 2.0$, estimated from kinetic data. ^f5 °C. ^g $I = 2.0$ M. ^h $I = 0.1$ M.

visible absorption spectrum of this product was identical with that of a product reprecipitated twice. Analyses. Found: C 12.24; H 4.60; N 14.31; Cl 13.80. Calc. for Cr₂C₈N₈H₃₆Cl₃O₁₈P: C 12.42; H 4.69; N 14.48; Cl 13.74. Spectral data are given in Table 1.

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