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Kinetics and mechanism of formation of 1:1 complex between chromium (III) with edta in aqueous acidic media

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ABSTRACT

The kinetics of the formation of 1:1 complex of chromium (III) with ethylenediaminetetraacetate (EDTA) was followed spectrophotometrically at $\lambda_{\max} = 552$ nm. The reaction was found to be first order in chromium (III). Increasing the edta concentration from 2.2×10^{-2} to 8.8 mol dm^{-3} accelerated the reaction rate. Increasing the pH from 3.3 to 4.7 also accelerate the reaction rate, while the reaction rate was retarded by increasing ionic strength and dielectric constant of the reaction medium. A mechanism was suggested to account for the results obtained which involves ion pair formation between the various species of the reactants. Value of $37.1 \pm 3 \text{ kJ mol}^{-1}$ was obtained for the energy of activation and $-195.6 \pm 6 \text{ K}^{-1} \text{ mol}^{-1}$ for the entropy of activation indicate an associative mechanism for the reaction. The logarithms of the formation constant of 1:1 complex formed were found to be 7.31.

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KEYWORDS

Kinetic;
Mechanism;
Substitution;
EDTA;
Chromium (III).

INTRODUCTION

In ligand substitution reactions which represent a major type of inorganic processes, one or more ligands around a metal ion are replaced by other ligands^[1]. Chromium (III) is classically known as a substitution-inert metal ion^[2].

Aminocarboxylate chelating agents complex strongly with most metals, thus altering metal bioavailability and mobility in the environment^[3]. These compounds are widely used for industrial, medical and agricultural purposes^[4-12]. These compounds are used as laundry detergent builders, boiler scale inhibitors, in metal plating and cleaning operations, in

textile manufacture, and in paper and cellulose industries. It is well known that Edta is a member of the aminocarboxylate family.

Although the experimental system and reaction studied here is very simple in nature, elucidation of the mechanism in this model system has implications for a variety of more complex homogeneous and heterogeneous phenomena involving metal-organic complexes (e.g., metal ion transport, bioavailability, and toxicity).

This study deals with the kinetic of complexation of chromium (III) with edta in weak acid solution. The study involves factors affecting the rate of reaction. The formation constant of the studied complex is also

measured.

EXPERIMENTAL

All chemicals were of pure grade and were used without further purification. Stock solution of (0.1 mol/dm) of hexa-aquachromium (III) was prepared by dissolving CrCl_3 in bidistilled water and leaving the solution for 48 hours at 45 °C, where upon green color of CrCl_3 changed to blue color of aquachromium (III)^[13]. All solutions were prepared using bidistilled water. The absorbance measurements were performed using thermostatted 292 Cecil spectrophotometer and pH measurements were conducted with Griffin pH meter fitted with glass-calomel electrode standardized by potassium hydrogen phthalate.

Kinetic experiments were conducted by mixing thermostatted solutions of chromium (III) with edta solution and adjusting hydrogen ion concentration to the required value with potassium hydroxide or perchloric acid. Ionic strength was adjusted by sodium perchlorate solution. The solution was then introduced into the reaction vessel, which was previously thermostatted to the desired temperature and the reaction was followed spectrophotometrically at $\lambda_{max} = 552 \text{ nm}$ for the complex formed. The reaction rate was followed under pseudo first order conditions where at least ten fold excess of the ligand concentration over the reactant chromium (III) concentration was always ensured. Values of the observed first order rate constant, k_{obs} , were determined graphically for each run by plotting $\log(A_\infty - A_t)$ versus time, t , where A denotes the measured absorbance and the subscripts refer to time of reaction. The absorbance (A_∞) was obtained directly after ensuring completion of the reaction. First order plots were linear for more than 85% of the reaction progress.

RESULTS AND DISCUSSION

The reaction was found to be first order in chromium (III), the observed first order rate constants, k_{obs} , did not vary with chromium (III) concentration, TABLE 1 ensuring first order kinetics in chromium (III).

The effect of varying edta concentration, at different pH values on the rate of reaction was also studied,

TABLE 1 and a plot of the first order rate constant, k_{obs} , against edta concentration was nonlinear, Figure 1, indicating formation of ion pair^[14,15].

Increasing the ionic strength, I , of the reaction medium from 0.7 to 1.25 mol/dm (adjusted by sodium perchlorate) the reaction rate TABLE 1. Applying *Bronsted Bjerrum* equation^[16,17], a linear relationship was obtained by plotting $\log k_{obs}$ versus \sqrt{I} , Figure 2 indicating that reaction involves ion pairing formation

The effect of the dielectric constant on the rate of reaction was studied using different ratios of ethanol-water mixtures. The values of the observed first order rate constant, k_{obs} increased with decreasing the dielectric constant of the reaction medium, ϵ , TABLE 1. Applying *Bjerrum's* equation^[18], a plot of $\log k_{obs}$ versus $1/\epsilon$ was linear with positive slopes, Figure 3 indicating that the reaction is an ion pair type^[19].

The effect of pH on the rate of reaction was studied in the range from 3.0 to 4.7 at various temperatures, TABLE 2. The results obtained show that the reaction is accelerated by lowering hydrogen ion concentration.

The dependence of k_{obs} on hydrogen ion concentration can be explained by in following equilibriums between the various species of each reactant which are present in the reaction medium^[20,21].

The penta-aquahydroxochromium (III) species is more reactive than the hexa-aquachromium (III) due to the presence of OH^- which causes an increase of water labilities due to its π -bonding ability^[22,23].

The results obtained can be explained by the following mechanism for the interaction between the predominant species of chromium (III) with the predominant species of edta in the pH range under investigation

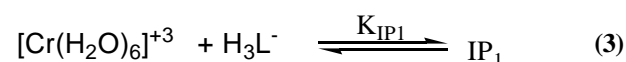
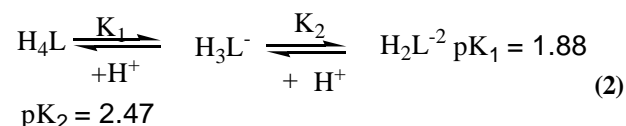
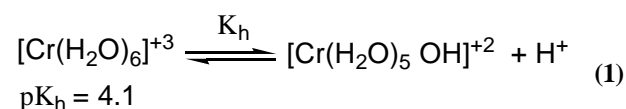
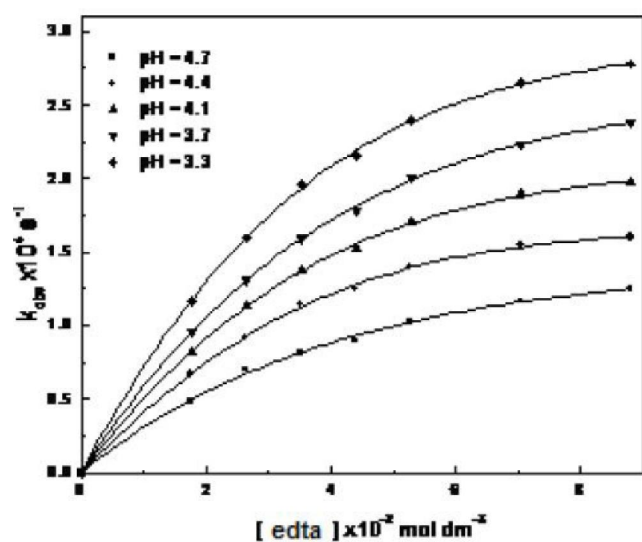
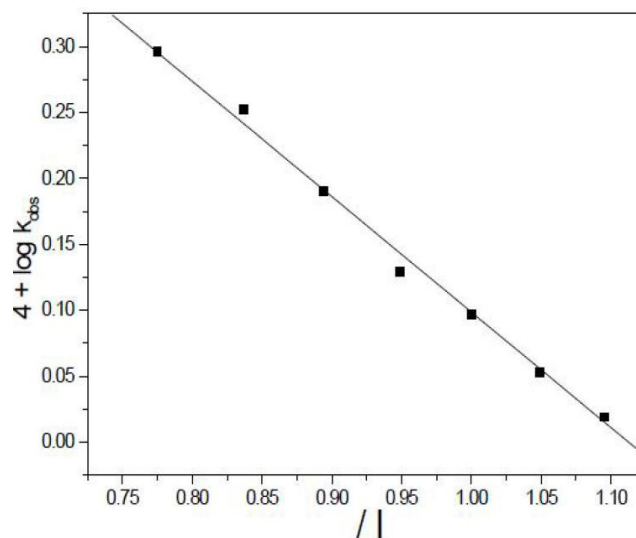


TABLE 1 : Values of k_{obs} under various conditions

[Cr(III)]x10 ³ Mol/dm	[edta]x10 ² Mol/dm	t °C	I mol/dm	ε	$k_{obs} \times 10^4 / s^{-1}$					
					pH					
					3.3	3.7	4.1	4.4	4.7	
4.4							1.959			
6.0							1.963			
7.2							1.971			
8.8	8.80	35	0.6				1.969			
10.4							1.977			
12.0							1.983			
13.6							1.975			
	1.76					0.482	0.670	0.817	0.957	1.168
	2.64					0.699	0.920	1.135	1.308	1.595
	3.52					0.815	1.139	1.380	1.593	1.960
	4.40	35	0.6			0.894	1.249	1.527	1.786	2.151
	5.28					1.026	1.396	1.698	2.007	2.399
	7.04					1.163	1.551	1.895	2.236	2.648
	8.80					1.250	1.599	1.975	2.379	2.779
			0.6					1.975		
			0.7					1.785		
			0.8					1.550		
8.8	8.80	35	0.9					1.346		
			1.0					1.251		
			1.1					1.131		
			1.2					1.045		
				78.00				1.234		
				75.32				1.287		
				72.63				1.353		
				69.95				1.433		
8.8	8.80	25	0.6					67.26		1.503
								64.58		1.591
								61.89		1.693
								59.21		1.819
								56.52		1.957

Figure 1 : Variation of k_{obs} with [edta] at various pH; $I = 0.6$ mol/dm, $t = 35$ °C, $[Cr(III)] = 8.8 \times 10^{-3}$ mol/dmFigure 2 : Variation of $\log k_{obs}$ with $1/[edta]$; $[edta] = 8.8 \times 10^{-2}$ mol/dm, $pH = 4.1$, $[Cr(III)] = 8.8 \times 10^{-3}$ mol/dm, $t = 35$ °C

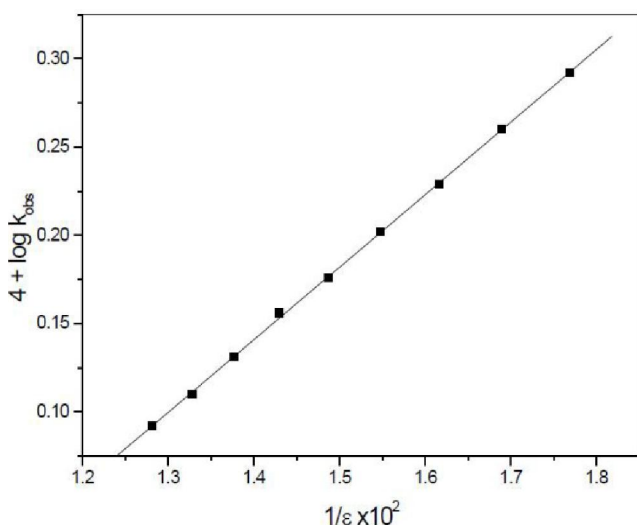


Figure 3 : Variation of $\log k_{obs}$ with $1/\epsilon$ in ethanol-water mixture; $t = 25^\circ\text{C}$, $\text{pH} = 4.1$, $[\text{Cr(III)}] = 8.8 \times 10^{-3} \text{ mol/dm}$, $I = 0.7 \text{ mol/dm}$, $[\text{edta}] = 8.8 \times 10^{-2} \text{ mol/dm}$

TABLE 2 : Kinetic data for the interaction of Cr (III) with edta at various temperature and proton concentration; $[\text{Cr(III)}] = 8.8 \times 10^{-3} \text{ mol/dm}$, $[\text{edta}] = 11 \times 10^{-2} \text{ mol/dm}$, $I = 0.6 \text{ mol/dm}$

pH	$k_{obs} \times 10^4 / \text{s}^{-1}$				
	25°C	30°C	35°C	40°C	45°C
3.3	0.766	1.012	1.250	1.531	2.007
3.7	1.007	1.257	1.539	2.019	2.530
4.1	1.234	1.567	1.975	2.475	3.125
4.4	1.475	1.853	2.379	3.009	3.764
4.7	1.703	2.164	2.785	3.508	4.355

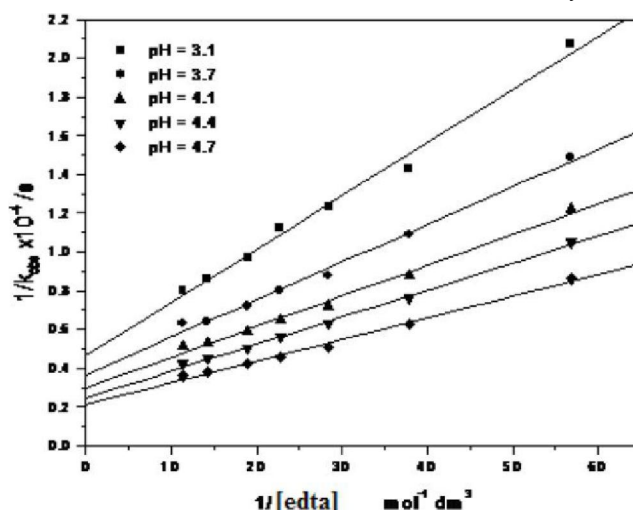
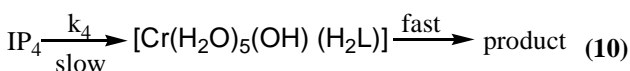
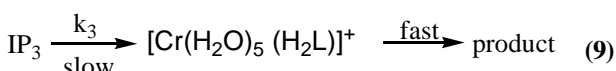
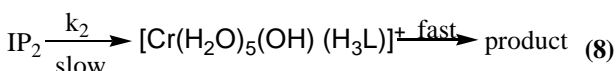
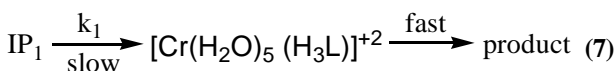
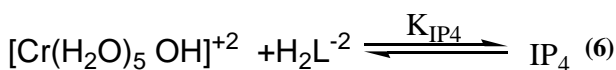
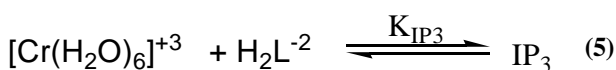
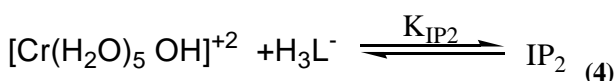


Figure 4 : Variation of $1/k_{obs}$ with $1/[\text{edta}]$; $[\text{Cr(III)}] = 8.8 \times 10^{-3} \text{ mol/dm}$, $t = 35^\circ\text{C}$, $I = 0.6 \text{ mol/dm}$, $\text{pH} = 4.1$

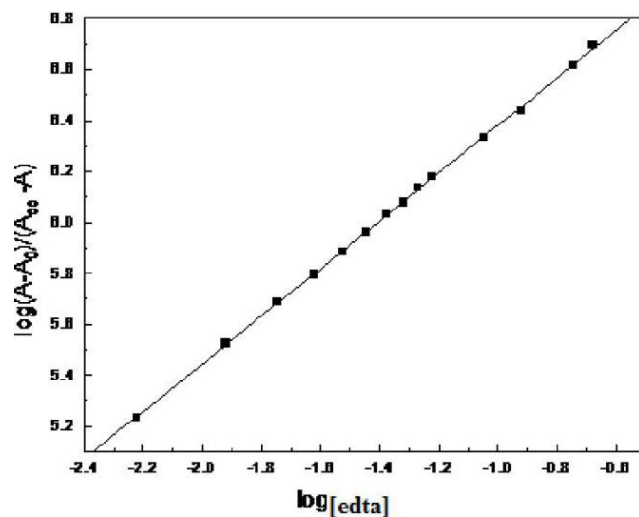


Figure 5 : Plot of $\log(A - A_0) / (A_\infty - A)$ vs $\log[\text{edta}]$; $I = 0.6 \text{ mol/dm}$, $\text{pH} = 4.1$, $[\text{Cr(III)}] = 8.8 \times 10^{-3} \text{ mol/dm}$, $t = 35^\circ\text{C}$

Where $\text{IP}_1 \equiv \{[\text{Cr}(\text{H}_2\text{O})_6]^{+3} \cdot \text{H}_3\text{L}^{-1}\}$, $\text{IP}_2 \equiv \{[\text{Cr}(\text{H}_2\text{O})_5 \text{OH}]^{+3} \cdot \text{H}_3\text{L}^{-1}\}$, $\text{IP}_3 \equiv \{[\text{Cr}(\text{H}_2\text{O})_6]^{+3} \cdot \text{H}_2\text{L}^{-2}\}$ $\text{IP}_4 \equiv \{[\text{Cr}(\text{H}_2\text{O})_5 \text{OH}]^{+2} \cdot \text{H}_2\text{L}^{-2}\}$

$\text{IP}_1 - \text{IP}_4$ are the hexa-aquo and penta-aquohydroxy ion pair complexes of chromium (III) and edta

The rate of exchange of the first ligand molecule, in the inner coordination sphere of the metal center is slow and therefore the rate determining equations (7-10)^[22]. As soon as one carboxyl group of the ligand enters into the inner sphere, the electron density on the chromium center increases owing to the inductive effect and as results the remaining ligands are labilized easily and its substitution is rapid. From the previous mechanism, the first order rate constant is derived as

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$$k_{obs} = \frac{(k_1 K_{IP1} [H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4} \frac{K_2 K_h}{[H^+]}) [edta]}{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]}) + ((K_{IP1} [H^+] + K_{IP2} K_2 + K_{IP3} K_h + K_{IP4} \frac{K_2 K_h}{[H^+]}) [edta])} \quad (11)$$

by inverting equation (11) we get equation

$$\frac{1}{k_{obs}} = \frac{K_{IP1} [H^+] + K_{IP2} K_2 + K_{IP3} K_h + K_{IP4} \frac{K_2 K_h}{[H^+]}}{(k_1 K_{IP1} [H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4} \frac{K_2 K_h}{[H^+]}) [edta]} + \frac{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]})}{(k_1 K_{IP1} [H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4} \frac{K_2 K_h}{[H^+]}) [edta]} \quad (12)$$

and a plot of $1/k_{obs}$ versus $1/[edta]$ gave straight line with slopes

$$S = \frac{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]})}{(k_1 K_{IP1} [H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4} \frac{K_2 K_h}{[H^+]})} \quad (13)$$

and intercepts, I

$$I = \frac{K_{IP1} [H^+] + K_{IP2} K_2 + K_{IP3} K_h + K_{IP4} \frac{K_2 K_h}{[H^+]}}{(k_1 K_{IP1} [H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4} \frac{K_2 K_h}{[H^+]})} \quad (14)$$

and

$$\frac{I}{S} = \frac{K_{IP1} [H^+] + K_{IP2} K_2 + K_{IP3} K_h + K_{IP4} \frac{K_2 K_h}{[H^+]}}{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]})} \quad (15)$$

The values of the ion pair formation constants, K_{IP} and the rate constants of the rate determining steps, k , were calculating by plotting $1/k_{obs}$ versus $1/[edta]$ at pH, 4.1, Figure 4. Values 7.11, 14.78, 10.15 and 16.81 $\text{mol}^{-1} \text{dm}^3$ for the ion pair formation constants, K_{IP} and 1.83, 4.81, 2.97 and $5.23 \times 10^{-3} \text{ s}^{-1}$ for the rate determining steps, k , respectively were calculating by applying equation (13-15) at different hydrogen ion concentrations and taking the values of K_1 , K_2 and K_h from equations (1,2)

The composition and formation constants of the complexes between chromium (III) and edta were determined using Hills equation (eq.16)^[23]

$$\log (A - A_0)/(A_\infty - A) = \log K + n \log [edta] \quad (16)$$

Where A is the absorbance reached at the end of the reaction, A_0 is the absorbance at zero edta concentration, and A_∞ is the equilibrium absorbance for highest concentration of edta. Plots of $\log (A - A_0)/(A_\infty - A)$ vs. $\log [edta]$, where [edta] is total concentration used, yield a straight line of slope = 1 (number of ligand molecules attached to one chromium atom) and intercept of $\log K = 11.3$ Figure 5.

REFERENCES

- [1] N.E.Brasch, D.A.Buckingham, C.R.Clark; J.Simpson, *Inorg.Chem.*, **35**, 7728 (1996).
- [2] H.L.Schalfer, G.Gliemann; *Basic Principles of Ligand Field Theory*, (Wiley-Interscience: New York) (1969).
- [3] B.Nowack; *Environ.Sc.Technol.*, **36**, 4009 (2002).
- [4] M.A.Carver, K.M.Humphrey, R.A.Patchett, C.W.Jones; *Eur.J.Biochem.*, **38(3)**, 611 (1984).
- [5] G.McLendon, H.Hull, K.Larkin, W.Chang; *J.Biol.Inorg.Chem.*, **4(2)**, 171 (1999).

- [6] S.Tandy, K.Bossart, R.Mueller, J.Ritschel, L.Hauser, R.Schulin, B.Nowak; *Environ.Sci. Technol.*, **38**, 937 (2004).
- [7] H.Yamanishi, S.Kimura, S.Inama, Y.Yamaguchi, T.Yanagihara; *Clin.Chem.*, **43(12)**, 2413 (1997).
- [8] H.J.Bolton, S.W.Li, D.J.Workman, D.C.Girvin; *J.Environ.Qual.*, **22**, 125 (1993).
- [9] C.A.Tolman; *Chem.Rev.*, **77**, 313 (1997).
- [10] O.Whiltaker, J.E.Vanderveen, M.J.Dinovi, P.M.Kusnesof, V.C.Dunkel; *Reg.Toxical.Pharm.*, **18**, 419 (1993).
- [11] M.E.Markowitz, P.E.Bifur, H.Ruff, J.F.Rosen; *Pediatrics*, **92**, 265 (1993).
- [12] W.H.Seegers; *Blood Clotting Enzymology*, (Academic Press: New York) (1967).
- [13] K.Emorson, W.M.Graven; *Inorg.Nucl.*, **11**, 309 (1959).
- [14] T.W.Swaddle; *Adv.Inorg.Bioinorg.Mech.*, **2**, 95 (1983).
- [15] T.W.Swaddle; *Rev.Phy.Chem.Jpn.*, **50**, 230 (1980).
- [16] F.Basolo, R.G.Pearson; *Mechanism of Inorganic reaction 1958* (2nd edn. Wiley: New York, Chapter 6) (1958).
- [17] A.A.Forst, R.G.Pearson; *Kinetic and Mechanism 1961* (John Wiley and Sons: New York, Ch 7) (1961).
- [18] M.Shahid, I.A.Khan, Kabir-ud-Din; *J.Chem.Soc. Dalton Trans.*, 3007 (1990).
- [19] K.Emorson, W.M.Graven; *J.Inorg.Nucl.Chem.*, **11**, 309 (1959).
- [20] P.Djudjevic, D.J.Radanovic, M.S.Cvijovic, D.Veselinovic; *Talanta.*, **38**, 460 (1991).
- [21] M.E.Mendola, T.Paul, T.J.Strathmann, R.F.Carbonaro; *Polyhedron*, **28**, 269 (2009).
- [22] B.Perlumutter-Hayman, F.Secco, E.Tapnhi, M.Venturini; *J.Chem.Soc.Dalton.Trans.*, 1124 (1980).
- [23] M.A.Abdullah, J.Barrett, P.O'Brien; *J.Chem.Soc. Dalton Trans.*, 1647 (1984).