Acta Chemica Scandinavica, 1999: 53: 1083 1092
Printed in UK. All rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Chromium(III) Complexes of the Hexadentate Ligand *N,N,N′,N′*-Tetrakis(2-pyridylmethyl)ethane-1,2-diamine. Synthesis, Structure and Reactivity

J. Eriksen,[a] P. Goodson,[b] A. Hazell,[c] D. J. Hodgson,[d] K. Michelsen,[a] O. Mønsted,[a] J. C. Rasmussen[a,*] and H. Toftlund[e]

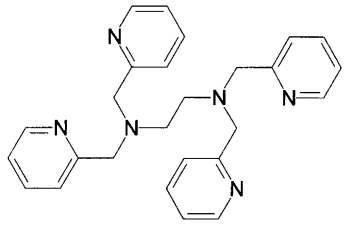
[a]Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 København Ø, Denmark, [b]University of Wyoming, Laramie, WY 82071, USA, [c]Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Århus, Denmark, [d]Academic Affairs, University of Nebraska at Omaha, 6001 Dodge Street, Omaha, NE 68182, USA and [e]Department of Chemistry, University of Odense, Campusvej 55, DK-5230 Odense M, Denmark

Eriksen, J., Goodson, P., Hazell, A., Hodgson, D. J., Michelsen, K., Mønsted, O., Rasmussen, J. C. and Toftlund, H., 1999. Chromium(III) Complexes of the Hexadentate Ligand *N,N,N′,N′*-Tetrakis(2-pyridylmethyl)ethane-1,2-diamine. Synthesis, Structure and Reactivity. – Acta Chem. Scand. 53: 1083–1092. © Acta Chemica Scandinavica 1999.

Chromium(III) complexes of *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethane-1,2-diamine, tpen, have been synthesised by air oxidation of chromium(II) acetate and the ligand in a methanol–water mixture. Addition of perchlorate precipitates $[Cr(tpen)(OCOCH_3)](ClO_4)_2 \cdot H_2O$, which has been used as the starting material for the synthesis of a number of complexes including $[Cr(tpen)](ClO_4)_3$, $[Cr(tpen)(OH)](ClO_4)_2$ and *cis*-$[Cr(tpen)(OH)_2]ClO_4 \cdot 3H_2O$. These compounds have all been characterised by single-crystal structure determinations. The four complexes are all monomeric and contain six-coordinate chromium(III) cations. In $[Cr(tpen)]^{3+}$ all six nitrogens of the potentially hexadentate tpen ligand are coordinated to chromium, in $[Cr(tpen)(OCOCH_3)]^{2+}$ and $[Cr(tpen)(OH)]^{2+}$ five nitrogen atoms are coordinated and in *cis*-$[Cr(tpen)(OH)_2]^+$ only four nitrogen atoms are coordinated. The remaining coordination sites in the last three cations are occupied by oxygen atoms of the acetate and the hydroxide ligands. In neutral solution the divalent base $[Cr(tpen)(OH)]^{2+}$ is relatively stable, but acidification leads to a fast equilibration reaction between $[Cr(tpen)(OH_2)]^{3+}$ and $[Cr(tpen)]^{3+}$, which has been characterized by stopped-flow measurements. In basic aqueous solution $[Cr(tpen)(OH)]^{2+}$ reacts slowly to give *cis*-$[Cr(tpen)(OH)_2]^+$. Acidification of *cis*-$[Cr(tpen)(OH)_2]^+$ solutions leads to the same hexaamine/pentaamine equilibrium mixture but by a considerably slower process. Part of this significant reactivity difference may be attributed to the conformation of the coordinated part of the ligand, which is similar in the hexaamine and pentaamine complexes, and markedly different in the tetraamine complex.

Hydrolytic metalloenzymes show a number of common features, including substrate polarisation and hydroxide activation often mediated through an extensive network of hydrogen bonds. In many cases these features are based upon metal ions with available coordination positions and uncoordinated bases close to the metal site.[1–4]

This work presents a number of chromium(III) complexes with a reasonably labile coordination position and one or more uncoordinated bases close to the metal centre. The work specifically deals with chromium(III) complexes of the *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-ethane-1,2-diamine ligand, tpen, which is shown in Fig. 1. The ligand is potentially a hexadentate ligand, but



tpen

Fig. 1. *N,N,N′,N′*-Tetrakis(2-pyridylmethyl)ethane-1,2-diamine (tpen).

because of the steric crowding in the hexaamine complex, pentaamine complexes with a wide variety of substituents are easily prepared.[5] Such complexes have obvious

* To whom correspondence should be addressed.

biomimetic qualifications, and the present contribution concentrates on structural features and the behaviour in aqueous solution of the hexaamine, pentaamine and tetraamine complexes.

Results and discussion

Preparations. Chromium(II) acetate reacts quickly with the tpen ligand in methanol–water mixtures. Air oxidation gives $[Cr(tpen)(OCOCH_3)]^{2+}$, which can be precipitated by addition of an excess of sodium perchlorate.[6] The acetate complex hydrolyses in weakly basic solution to give $[Cr(tpen)(OH)]^{2+}$, which may also be precipitated as a perchlorate salt. Acidification of $[Cr(tpen)(OH)]^{2+}$ solutions with perchloric acid gives the hexaamine complex $[Cr(tpen)](ClO_4)_3$. Prolonged standing of $[Cr(tpen)(OH)]^{2+}$ in dilute sodium hydroxide gives solutions of *cis*-$[Cr(tpen)(OH)_2]^+$, which may be precipitated as a perchlorate salt by concentration of the solution.

Description of the structures. The cations of the four hexaamine-, pentaamine- and tetraaminechromium(III) perchlorate salts are shown in Fig. 2. All four cations have an approximate octahedral coordination of the chromium central atom, with coordination to two amine nitrogen atoms and two pyridine nitrogen atoms in *trans* position to each other. The remaining two coordination sites are occupied by pyridine nitrogen atoms or oxygen atoms from acetate or hydroxide ligands. Principal bond lengths and angles are summarized in Table 1, and individual structural features are described below.

$[Cr(tpen)](ClO_4)_3$. The structure consists of $[Cr(tpen)]^{3+}$ cations and perchlorate anions. Two of the perchlorate anions are disordered, and were fitted to a model in which two unequally occupied sets of oxygen atom positions share a common Cl O bond, Cl(2)–O(8) and Cl(3)–O(12), giving rise to two approximate tetrahedra which are rotated by about 60° from each other. This type of disorder is well known for perchlorate anions.

$[Cr(tpen)(OH)](ClO_4)_2$. The structure consists of $[Cr(tpen)(OH)]^{2+}$ cations and perchlorate anions. The Cr–O distance of 1.845(3) Å is very short, and is almost 0.05 Å shorter than those in *cis*-$[Cr(tpen)(OH)_2]^+$. One of the perchlorate anions is disordered in such a way that all four oxygen atoms are occupying two distinct positions, leading to two separate tetrahedra centred on Cl(2).

$[Cr(tpen)(OCOCH_3)](ClO_4)_2 \cdot H_2O$. The structure consitsts of $[Cr(tpen)(OCOCH_3)]^{2+}$ cations, perchlorate anions and water of crystallization. The water molecule is weakly hydrogen bonded to both perchlorate ions with O(11)···O(3)=2.817(5) Å and O(11)···O(8)= 3.068(6) Å.

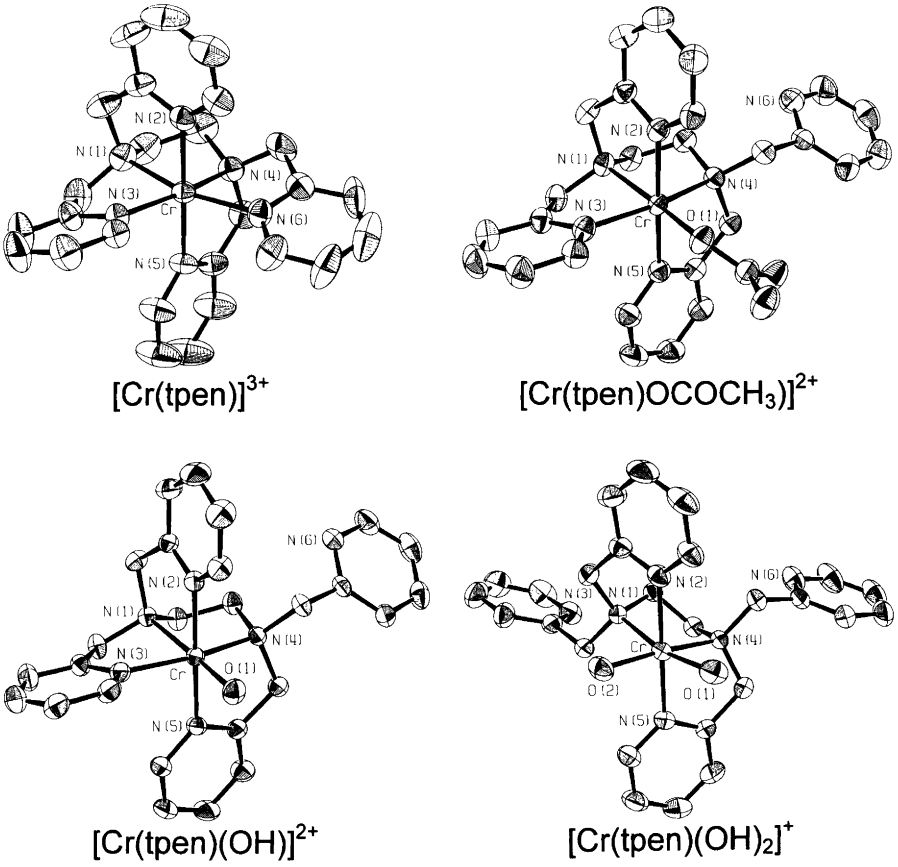


Fig. 2. ORTEP[7] drawings of the four cations, with thermal ellipsoids drawn at the 50% probability level.

Table 1. Comparison of bond lengths (in Å) and bond angles (in °) for the four chromium complexes presented.

	$[Cr(tpen)(OCOCH_3)]^{2+}$	$[Cr(tpen)]^{3+}$	$[Cr(tpen)(OH)]^{2+}$	$[Cr(tpen)(OH)_2]^{+}$
Cr–N1	2.092(2)	2.039(4)	2.112(2)	2.166(2)
Cr–N2	2.049(2)	2.044(4)	2.055(2)	2.067(2)
Cr–(N3/O2)	2.056(2)	2.046(4)	2.045(2)	1.895(2)
Cr–N4	2.137(2)	2.059(4)	2.128(2)	2.168(2)
Cr–N5	2.064(2)	2.039(4)	2.073(2)	2.064(2)
Cr–(N6/O1)	1.916(2)	2.063(5)	1.845(3)	1.894(2)
N(1)–Cr–N2	81.79(8)	82.5(2)	81.5(1)	78.56(7)
N(1)–Cr–(N3/O2)	78.92(8)	79.4(2)	79.1(1)	90.70(7)
N(1)–Cr–N4	84.84(8)	85.7(2)	84.2(1)	82.63(6)
N(1)–Cr–N5	93.95(9)	96.1(2)	92.2(1)	96.81(6)
N(1)–Cr–(O1/N6)	168.82(8)	163.9(2)	174.5(1)	166.80(7)
N(2)–Cr–(N3/O2)	93.10(8)	89.0(2)	89.8(1)	90.41(7)
N(2)–Cr–N4	92.18(8)	97.6(2)	93.6(1)	97.80(7)
N(2)–Cr–N5	173.02(7)	178.5(2)	172.3(1)	174.38(7)
N(2)–Cr–(O1/N6)	91.26(8)	92.8(2)	95.9(1)	92.40(8)
N(3)–Cr–N4	162.02(8)	162.8(2)	162.2(1)	168.15(7)
N(3)–Cr–N5	91.49(9)	91.2(2)	93.5(1)	92.85(7)
N(3)–Cr–(O1/N6)	92.80(8)	116.0(2)	96.3(1)	99.04(9)
N(4)–Cr–N5	81.89(8)	81.9(2)	81.2(1)	78.32(6)
N(4)–Cr–(O1/N6)	104.26(8)	79.6(2)	100.7(1)	89.18(8)
N(5)–Cr–(O1/N6)	93.76(8)	88.5(2)	90.7(1)	91.61(8)

cis-*[Cr(tpen)(OH)$_2$](ClO$_4$)·3H$_2$O*. The structure consists of $[Cr(tpen)(OH)_2]^+$ cations, perchlorate anions and water of crystallization. The hydroxide ligands are *cis* to each other and *trans* to the amine nitrogens. The hydroxide ligands are hydrogen-bonded to water molecules with O(1)···O(8)=2.771(3) Å and O(2)···O(9) =2.704(3) Å.

Cr–N distances in the four complexes are in the range 2.039(4)–2.168(4) Å, with a mean value of 2.078(8) Å; the figure in parentheses denotes the sample standard deviation of the mean. The Cr–N(pyridine) distances are in the range 2.039(4)–2.073(2) Å with a mean value, 2.055(8) Å, which as expected is shorter than that of 2.113(14) Å for Cr–N(amine) bonds. There is, however, a very large spread of Cr–N(amine) values, 2.039(4)–2.168(2) Å, and for the hexaamine complex there is no significant difference between the two types of bonds.

The N–Cr–N angles of the five-membered chelate rings range from 78.3(1) to 82.5(1), mean 80.3(4)°, for the picolylamine units and from 82.6(1) to 85.7(2), mean 84.3(5)°, for the ethane-1,2-diamine units. The hexaamine cation is seen to be highly strained, in particular the angle N(3)–Cr–N(6) is widened out to 116.0(2)°. It should be noted that it is one or both of these nitrogen atoms which becomes detached in the pentaamine- and tetraamine complexes.

Reactivity. $[Cr(tpen)(OH)]^{2+}$ is reasonably stable in basic and neutral solution. Extrapolation of kinetic data in basic solution at higher temperatures to 25 °C gives a rate constant of $3.8(3)\times10^{-5}\,s^{-1}$ for the dominant hydroxide independent path of the proces:

$$[Cr(tpen)(OH)]^{2+} + H_2O \rightarrow \textit{cis}\text{-}[Cr(tpen)(OH)_2]^{+} + H^{+}$$

corresponding to a half-life of about 5 h.

Addition of acid to $[Cr(tpen)(OH)]^{2+}$ reveals a behaviour as a divalent base, with apparent acidity constants $K_{a1,obs}=0.32(2)$ M and $K_{a2,obs}=10^{-4.065(5)}$ M for the diprotonated complex at 25 °C in 1 M $NaClO_4$. These constants were determined spectrophotometrically, cf. Fig. 3, and by glass electrode measurements.

Monitoring the addition of acid to $[Cr(tpen)(OH)]^{2+}$ by stopped-flow measurements reveal a fast first-order

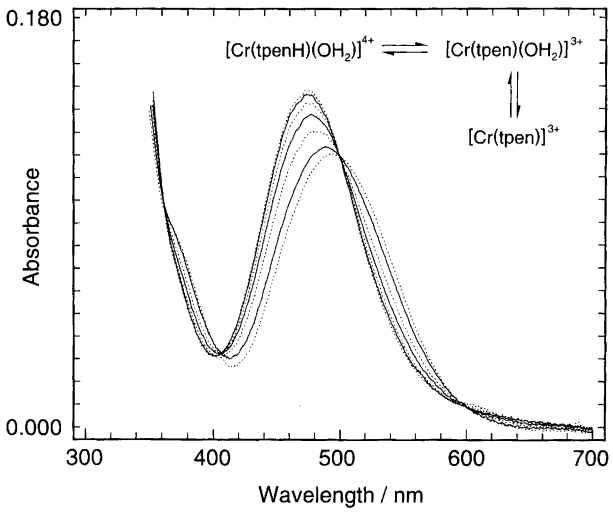


Fig. 3. Visible absorption spectra of 0.748 mM solutions of [Cr(tpen)-complexes in 1 M [Na/H]ClO_4 as function of the hydrogen ion concentration: $0.01<[H^+]<1.00$ M.

reaction with a rate constant that is dependent on the hydrogen ion concentration. Similar fast first-order reactions are observed when solutions of $[Cr(tpen)]^{3+}$ at intermediate hydrogen ion concentrations, 10^{-3}–10^{-2} M, are made more acidic or basic. The hydrogen ion concentration dependence of the reaction rates in acidic and basic solution is shown in Fig. 4. This dependence may be described by:

$$k_{obs} = k^{+} + \frac{k^{-}K_{a1}[H^{+}]^{-1}}{1 + K_{a1}[H^{+}]^{-1} + K_{a1}K_{a2}[H^{+}]^{-2}} \qquad (1)$$

corresponding to the reaction scheme given in Scheme 1. The acidity constants $K_{a1,obs}$ and $K_{a2,obs}$ were measured by methods sufficiently slow for the hexaamine–pentaamine equilibrium to be established during the measurements. Interpreted within Scheme 1 they are consequently given by:

$$K_{a1,obs} = \frac{K_{a1}(k^{+} + k^{-})}{k^{+}}$$

$$K_{a2,obs} = \frac{K_{a2}k^{+}}{k^{+} + k^{-}}$$

Acidification of *cis*-$[Cr(tpen)(OH)_2]^{+}$ solutions lead to the same equilibrium mixture of hexaamine and pentaamine complexes, but by a considerably slower process. Part of this significant reactivity difference may be attributed to differences in the conformation of the coordinated part of the ligand, particularly of the ethane-1,2-diamine unit, which, as shown in Fig. 2, is similar in the hexaamine and pentaamine complexes, and markedly different in the tetraamine complex.

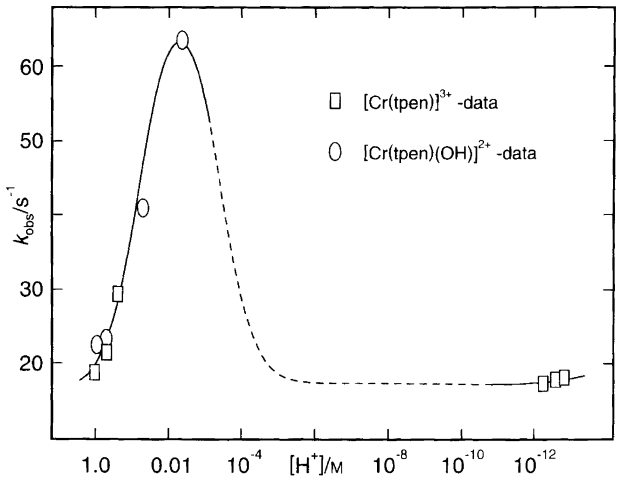
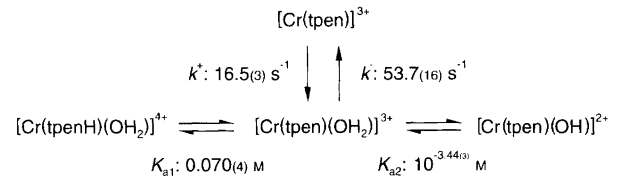


Fig. 4. Observed and calculated first order rate constants for equilibration between Cr(tpen) complexes as a function of the hydrogen ion concentration, cf. Scheme 1, eqn. (1) and the text. The slight increase in rate in basic solution is ascribed to a medium effect.[8]



Scheme 1.

Experimental

CAUTION! All the perchlorate salts are potentially explosive, and should be handled with care.

N,N,N′,N′-*Tetrakis(2-pyridylmethyl)ethane-1,2-diamine*, tpen, was prepared by a modification of the literature method given in Ref. 6: 2-pyridinecarbaldehyde 10.9 g (100 mmol) was added to a solution of ethane-1,2-diamine 3.3 g (50 mmol) in 40 ml of ethanol at room temperature. This mixture was heated to boiling, refluxed for 10 min, and then cooled to room temperature. The reaction mixture was evaporated to dryness on a rotary evaporator at 40 °C, then re-dissolved in 50 ml of abs. ethanol. Reduction with sodium tetrahydridoborate 5.0 g (0.132 mmol), was accomplished by the addition of small portions of the solid reductant over 3 h, keeping the temperature at about 50 °C. The reaction mixture was left overnight at room temperature, then heated to the boiling point. After the reaction mixture had been cooled to room temperature, 15 ml of 12 M hydrochloric acid were added, to remove traces of sodium tetrahydridoborate. Then 20 ml of 5 M sodium hydroxide were added to neutralise the excess acid. The solution was filtered and the volume reduced to one third on a rotary evaporator at 60 °C. After being cooled, the resulting *N,N′*-bis(2-pyridylmethyl)ethane-1,2-diamine solution was extracted three times with 50 ml of chloroform. The combined chloroform phases were dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The resulting crude product was dissolved in 40 ml of methylene chloride, and mixed with a solution of sodium hydroxide 8 g (200 mmol) and tetraethyl ammonium bromide 0.21 g (0.1 mmol) in 20 ml of water. The mixture was cooled to 5 °C, and 2-chloromethylpyridine hydrochloride 12.8 g (100 mmol) in 20 ml of water was slowly added under vigorous stirring keeping the temperature at 5 °C. This mixture was left with vigorous stirring, at 5 °C for 10 days. The use of this low reaction temperature gives a much higher yield than a faster reaction at higher temperature. When the reaction was completed the phases were separated and the aqueous phase was extracted twice with 50 ml of methylene chloride. The combined organic phases were dried over anhydrous sodium sulfate, filtered and evaporated to dryness. Two portions of 100 ml abs. ethanol were added and removed by evaporation, which eases crystallization of the viscous fluid, which was left overnight at −20 °C. The resulting solid was crushed and washed twice with 25 ml of ice cold acetone on a filter. Yield 11 g (50%). Another crop of crystals could be won by evaporation of the combined mother liquour and the acetone washings as described above. Total yield 15.5 g (71%). Analyses: N, C and H. NMR shows only one product.

[Cr(tpen)(OCOCH$_3$)](ClO$_4$)$_2$·H$_2$O, tpen, 6.18 g (14.6 mmol), was dissolved in 30 ml of methanol at room temperature, 70 ml of water were added, and the resulting solution was degassed by 3 freeze–pump–thaw cycles. Chromium(II) acetate dihydrate, 3.0 g (14.6 mmol), was added to the frozen solution. The mixture was heated to 50 °C and stirred, first under nitrogen for 1 h, and next for 3 h, still at 50 °C, in an open flask, to allow for oxidation by air. 28 ml of saturated sodium perchlorate was added and the reaction mixture left overnight for precipitation of [Cr(tpen)(OCOCH$_3$)](ClO$_4$)$_2$·H$_2$O. The crystals were filtered of and washed twice with 5 ml of ice cold water. Yield 9.0 g (95%). Recrystallization was done by dissolving the crude product in the minimum amount of a cold 1 : 4 water–acetonitrile mixture. This solution was filtered and left at room temperature for solvent evaporation and precipitation of the pure product, which was isolated as described above. Analyses: Cr, N, C, H and Cl.

[Cr(tpen)](ClO$_4$)$_3$. [Cr(tpen)(OCOCH$_3$)](ClO$_4$)$_2$·H$_2$O, 5.0 g (7.7 mmol), was dissolved in 25 ml of water and sodium hydroxide, 0.62 g (15 mmol), was added. The solution was heated to the boiling point then cooled to room temperature and acidified to a hydrogen ion concentration of about 0.1 M by the addition of 70% perchloric acid, 2.1 ml (25 mmol). The solution was left for precipitation overnight to give [Cr(tpen)](ClO$_4$)$_3$. The crystals were filtered of and washed twice with 5 ml of ice cold acetone. Yield 5.3 g (92%). Recrystallization was done by dissolving the crude product in the minimum amount of boiling 0.1 M perchloric acid, cooling and isolation as described above. Analyses: Cr, N, C and H.

[Cr(tpen)(OH)](ClO$_4$)$_2$. [Cr(tpen)(OCOCH$_3$)](ClO$_4$)$_2$·H$_2$O, 5 g (7.7 mmol), was dissolved in 25 ml of water and sodium hydroxide 0.62 g (15.4 mmol) was added. The solution was heated to the boiling point then cooled to room temperature, neutralised with perchloric and left overnight to precipitate the product. The crystals were filtered of and washed twice with 5 ml of ice cold water. Yield 4.5 g, 85%. Recrystallization was done by

Table 2. Crystal and experimental data for [Cr(tpen)(OCOCH$_3$)](ClO$_4$)$_2$·H$_2$O (**1**), [Cr(tpen)](ClO$_4$)$_3$ (**2**), [Cr(tpen)(OH)](ClO$_4$)$_2$ (**3**) and [Cr(tpen)(OH)$_2$](ClO$_4$)·3H$_2$O (**4**).

	1	**2**	**3**	**4**
Formula weight	752.54	774.89	692.45	664.09
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
Unit-cell dimensions:				
a/Å	12.414(3)	9.780(2)	9.457(2)	9.6166(5)
b/Å	10.740(2)	18.702(4)	10.646(2)	16.119(1)
c/Å	13.682(3)	18.323(4)	14.545(3)	19.445(1)
α/°	75.05(1)	90.0	93.22(3)	90.0
β/°	109.38(1)	93.78(3)	94.60(3)	90.0
γ/°	109.60(1)	90.0	99.87(3)	90.0
V/Å^3	1598.9(6)	3344(1)	1434.4(5)	3014.2(2)
Z	2	4	2	4
F(000)	778	1588	714	1388
T/K	294	293	293	298
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Linear absorption coefficient/cm^{-1}	0.583	0.640	0.650	0.517
Absorption correction	Integration	None	None	Integration
Intensity data collection:				
Crystal size/mm	0.87 × 0.66 × 0.17	0.38 × 0.26 × 0.11	0.44 × 0.25 × 0.20	0.40 × 0.18 × 0.16
Range of *h*	0–15	0–11	0–12	−12–12
Range of *k*	−13–12	0–21	−13–13	−21–21
Range of *l*	−16–16	−21–21	−18–18	−26–26
Range of θ°	1.8–27.0	2.0–25.0	2.0–27.5	2.1–28.4
Reflections collected	6549	6401	6984	19738
Independent reflections	6113	5891	6584	7160
R_{int}	0.012	0.053	0.026	0.033
Reflections with $I > N\sigma(I)$, *N*	4770(3)	5887(2)	5081(2)	6349(3)
Structure refinement:				
R	0.037	0.069	0.050	0.034
wR	0.051	0.100	0.102	0.040
Goodness of fit, *S*	1.240	1.533	1.171	2.077
Data/restraints/parameters	4770/0/442	5887/0/489	5081/0/438	6349/0/413
Largest different peak and hole	0.43, −0.45	0.39, −0.49	0.62, −0.46	1.40, −0, −0.50
Weighting scheme	$W = 1/\{[\sigma(F^2) + 1.03F^2]^{1/2} - \lvert F\rvert\}^2$ for all structures			

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters for $[Cr(tpen)(OCOCH_3)](ClO_4)_2$ (**1**).

Atom	*x*	*y*	*z*	$U_{eq}/Å^2$
Cr	0.77427(3)	0.23147(4)	0.26957(3)	0.0257(2)
Cl(1)	0.67739(6)	−0.30050(7)	0.12787(5)	0.0439(4)
Cl(2)	1.27027(6)	0.54369(8)	0.36418(6)	0.0471(5)
N(1)	0.6561(2)	0.1988(2)	0.1227(2)	0.034(1)
N(2)	0.8465(2)	0.4067(2)	0.1820(2)	0.032(1)
N(3)	0.6386(2)	0.2989(2)	0.2718(2)	0.035(1)
N(4)	0.8707(2)	0.1251(2)	0.2339(2)	0.031(1)
N(5)	0.7031(2)	0.0433(2)	0.3449(2)	0.035(1)
N(6)	1.0613(2)	0.1050(3)	0.1371(2)	0.052(2)
C(1)	0.6797(2)	0.0866(3)	0.0949(2)	0.038(2)
C(2)	0.8126(2)	0.1125(3)	0.1198(2)	0.037(2)
C(3)	0.6754(3)	0.3244(3)	0.0432(2)	0.040(2)
C(4)	0.7914(2)	0.4238(3)	0.0788(2)	0.036(2)
C(5)	0.8371(3)	0.5340(3)	0.0105(2)	0.053(2)
C(6)	0.9387(3)	0.6295(4)	0.0510(3)	0.060(2)
C(7)	0.9934(3)	0.6123(3)	0.1568(3)	0.052(2)
C(8)	0.9460(2)	0.4998(3)	0.2204(2)	0.039(2)
C(9)	0.5336(2)	0.1633(3)	0.1351(2)	0.039(2)
C(10)	0.5338(2)	0.2565(3)	0.2008(2)	0.037(2)
C(11)	0.4345(3)	0.2931(3)	0.1936(3)	0.048(2)
C(12)	0.4425(3)	0.3726(4)	0.2620(3)	0.056(2)
C(13)	0.5484(3)	0.4148(3)	0.3345(3)	0.051(2)
C(14)	0.6459(3)	0.3781(3)	0.3372(2)	0.040(2)
C(15)	0.8561(2)	−0.0104(2)	0.3018(2)	0.035(2)
C(16)	0.7538(2)	−0.0521(2)	0.3491(2)	0.034(1)
C(17)	0.7183(3)	−0.1818(3)	0.4005(2)	0.043(2)
C(18)	0.6285(3)	−0.2159(3)	0.4487(2)	0.052(2)
C(19)	0.5766(3)	−0.1178(3)	0.4450(3)	0.053(2)
C(20)	0.6153(3)	0.0084(3)	0.3933(2)	0.045(2)
C(21)	1.0022(2)	0.1951(3)	0.2509(2)	0.037(2)
C(22)	1.0734(2)	0.1151(3)	0.2357(2)	0.036(2)
C(23)	1.1478(3)	0.0552(4)	0.3206(3)	0.055(2)
C(24)	1.2110(3)	−0.0164(4)	0.3027(3)	0.068(3)
C(25)	1.1992(3)	−0.0273(4)	0.2027(4)	0.063(3)
C(26)	1.1239(3)	0.0344(4)	0.1228(3)	0.064(3)
O(1)	0.8750(2)	0.2940(2)	0.3976(1)	0.038(1)
C(27)	0.9430(2)	0.2409(3)	0.4815(2)	0.038(2)
C(28)	0.9888(3)	0.3166(3)	0.5712(2)	0.052(2)
O(2)	0.9675(2)	0.1384(2)	0.4871(2)	0.058(2)
O(3)	0.5993(3)	−0.2501(4)	0.1535(3)	0.095(3)
O(4)	0.6121(3)	−0.4142(3)	0.0793(3)	0.081(2)
O(5)	0.7635(3)	−0.3322(4)	0.2200(3)	0.088(3)
O(6)	0.7307(3)	−0.1966(3)	0.0561(3)	0.092(3)
O(7)	1.3881(2)	0.5330(3)	0.4128(2)	0.068(2)
O(8)	1.2692(4)	0.6792(3)	0.3423(4)	0.103(3)
O(9)	1.1969(3)	0.4715(4)	0.4319(3)	0.100(3)
O(10)	1.2238(3)	0.4902(5)	0.2689(3)	0.103(3)
O(11)	1.4166(3)	0.8231(3)	0.1843(2)	0.074(2)

dissolving the crude product in the minimum of boiling water, filtration, cooling, precipitation with excess sodium perchlorate and isolation as described above. Analyses: Cr, N, C and H.

cis-*[Cr(tpen)(OH)$_2$]ClO$_4$·3H$_2$O.* [Cr(tpen)(OH)]-$(ClO_4)_2$, 5.0 g (7.2 mmol), was dissolved in 30 ml of 0.1 M sodium hydroxide at room temperature. The solution was left overnight and the volume reduced to one half on a rotary evaporator at 60 °C. Cooling to room temperature gave precipitation of *cis*-$[Cr(tpen)(OH)_2]ClO_4 \cdot 3H_2O$. The crystals were filtered of and washed twice with 5 ml of ice cold acetone. Yield 3.0 g (69%). Recrystallization was done by dissolving the crude product in the minimum amount of 0.1 M sodium hydroxide at 60 °C, cooling to room temperature and isolation as described above. Analyses: Cr, N, C, H and Cl.

X-Ray structure determinations. The structures of the four complexes: $[Cr(tpen)(OCOCH_3)](ClO_4)_2 \cdot H_2O$ (**1**), $[Cr(tpen)](ClO_4)_3$ (**2**), $[Cr(tpen)(OH)](ClO_4)_2$ (**3**) and *cis*-$[Cr(tpen)(OH)_2](ClO_4) \cdot 3H_2O$ (**4**) were determined at room temperature. Data for **1** were collected on a Huber four-circle diffractometer, **2** and **3** on a Siemens P3 diffractometer and **4** on a Siemens SMART

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters for [Cr(tpen)]$(ClO_4)_3$ (**2**).

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Cr	0.1196(1)	0.2922(1)	0.2822(1)	0.032(1)
N(1)	−0.0370(4)	0.3509(3)	0.2338(3)	0.044(1)
N(2)	0.1206(5)	0.3725(2)	0.3579(2)	0.038(1)
N(3)	0.2254(4)	0.3576(2)	0.2163(2)	0.034(1)
N(4)	−0.0316(5)	0.2306(2)	0.3237(3)	0.042(1)
N(5)	0.1135(4)	0.2130(3)	0.2056(2)	0.040(1)
N(6)	0.2366(5)	0.2258(2)	0.3511(2)	0.043(1)
C(1)	−0.1651(5)	0.3074(3)	0.2390(4)	0.062(2)
C(2)	−0.1579(6)	0.2756(4)	0.3156(4)	0.067(2)
C(3)	−0.0489(6)	0.4225(3)	0.2693(4)	0.059(2)
C(4)	0.0398(6)	0.4291(3)	0.3392(3)	0.047(2)
C(5)	0.0405(7)	0.4903(4)	0.3818(5)	0.071(2)
C(6)	0.1251(8)	0.4939(4)	0.4435(5)	0.081(3)
C(7)	0.2086(7)	0.4382(4)	0.4635(4)	0.068(2)
C(8)	0.2058(6)	0.3778(4)	0.4213(3)	0.053(2)
C(9)	−0.0025(6)	0.3619(3)	0.1566(3)	0.059(2)
C(10)	0.1458(6)	0.3842(3)	0.1597(3)	0.046(2)
C(11)	0.2023(8)	0.4269(4)	0.1079(4)	0.075(2)
C(12)	0.3368(8)	0.4443(4)	0.1152(4)	0.075(2)
C(13)	0.4175(7)	0.4185(4)	0.1741(4)	0.062(2)
C(14)	0.3581(6)	0.3754(3)	0.2244(3)	0.042(2)
C(15)	−0.0495(6)	0.1613(3)	0.2838(3)	0.052(2)
C(16)	0.0273(6)	0.1592(3)	0.2162(3)	0.046(2)
C(17)	0.0071(7)	0.1042(4)	0.1683(4)	0.076(2)
C(18)	0.0836(8)	0.1012(4)	0.1072(5)	0.103(3)
C(19)	0.1762(8)	0.1547(4)	0.0979(4)	0.090(3)
C(20)	0.1902(6)	0.2088(4)	0.1473(3)	0.061(2)
C(21)	0.0162(6)	0.2175(3)	0.4019(3)	0.058(2)
C(22)	0.1633(7)	0.1951(3)	0.4030(3)	0.051(2)
C(23)	0.2243(10)	0.1459(4)	0.4519(4)	0.080(2)
C(24)	0.3591(10)	0.1291(5)	0.4460(5)	0.101(3)
C(25)	0.4318(8)	0.1590(4)	0.3920(5)	0.087(3)
C(26)	0.3670(6)	0.2081(4)	0.3452(4)	0.063(2)
Cl(1)	0.1171(2)	0.0960(1)	−0.1056(1)	0.055(1)
O(1)	0.2514(4)	0.1040(3)	−0.0699(2)	0.085(2)
O(2)	0.0542(5)	0.1626(3)	−0.1117(3)	0.112(2)
O(3)	0.1284(5)	0.0679(3)	−0.1776(3)	0.103(2)
O(4)	0.0422(5)	0.0482(3)	−0.0631(3)	0.108(2)
Cl(2)	0.2531(2)	0.4700(1)	0.9008(1)	0.056(1)
O(5)	0.1367(5)	0.4897(3)	0.9370(3)	0.100(2)
O(6A)	0.2594(10)	0.4841(7)	0.8281(5)	0.103(5)
O(7A)	0.2577(9)	0.3939(4)	0.9125(6)	0.102(4)
O(8A)	0.3678(12)	0.4971(8)	0.9432(6)	0.149(7)
O(6B)	0.2841(16)	0.5476(9)	0.8826(13)	0.081(9)
O(7B)	0.1987(21)	0.4376(13)	0.8371(13)	0.091(9)
O(8B)	0.3660(24)	0.4426(12)	0.9322(11)	0.077(9)
Cl(3)	0.4086(2)	0.7928(1)	0.8851(1)	0.074(1)
O(9)	0.4956(6)	0.8291(4)	0.9357(3)	0.146(3)
O(10A)	0.4613(20)	0.7493(12)	0.8318(14)	0.168(13)
O(11A)	0.3568(26)	0.8497(11)	0.8473(15)	0.217(14)
O(12A)	0.3035(15)	0.7599(9)	0.9178(7)	0.116(8)
O(10B)	0.4500(40)	0.7256(11)	0.9116(12)	0.240(19)
O(11B)	0.4484(34)	0.7891(20)	0.8188(9)	0.143(16)
O(12B)	0.2822(32)	0.8158(30)	0.8843(26)	0.382(38)

diffractometer.[9] Crystal data and experimental parameters are presented in Table 2. The data were corrected for Lorentz-polarization effects, absorption corrections were made by integration for **1** and **4**. The structures were solved by direct methods and refined by least-squares techniques using programs from the SHELXTL system[10] for **2** and **3** and from the KRYSTAL[11] package for **1** and **4**. Atomic scattering factors were taken from Ref. 12 for **1** and **4** and from Ref. 13 for **2** and **3**. Positional parameters and equivalent isotropic displacement parameters for the four structures are listed in Tables 3–6.

[Cr(tpen)(OCOCH$_3$)](ClO$_4$)$_2$·H$_2$O. The complex crystallizes in the centrosymmetric triclinic space-group $P\bar{1}$ with two molecules in the unit cell. All non-hydrogen atoms were refined anisotropically, hydrogen atoms of

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters for $[Cr(tpen)(OH)](ClO_4)_2$ (**3**).

Atom	*x*	*y*	*z*	$U_{eq}/Å^2$
Cr	0.3382(1)	0.6884(1)	0.2921(1)	0.022(1)
N(1)	0.4312(2)	0.7001(2)	0.1649(2)	0.024(1)
N(2)	0.2093(2)	0.5325(2)	0.2210(2)	0.026(1)
N(3)	0.4976(3)	0.5827(2)	0.3139(2)	0.028(1)
N(4)	0.2135(2)	0.8200(2)	0.2374(2)	0.024(1)
N(5)	0.4679(3)	0.8572(2)	0.3472(2)	0.027(1)
N(6)	−0.0734(3)	0.8326(3)	0.0987(2)	0.038(1)
O(1)	0.2619(3)	0.6635(3)	0.4039(2)	0.037(1)
C(1)	0.4082(3)	0.8257(3)	0.1311(2)	0.028(1)
C(2)	0.2527(3)	0.8375(3)	0.1403(2)	0.031(1)
C(3)	0.3612(3)	0.5907(3)	0.0982(2)	0.032(1)
C(4)	0.2307(3)	0.5129(3)	0.1318(2)	0.027(1)
C(5)	0.1417(4)	0.4182(3)	0.0745(2)	0.041(1)
C(6)	0.0323(4)	0.3419(4)	0.1113(3)	0.054(1)
C(7)	0.0138(4)	0.3583(3)	0.2033(3)	0.052(1)
C(8)	0.1033(4)	0.4548(3)	0.2570(2)	0.037(1)
C(9)	0.5869(3)	0.6954(3)	0.1851(2)	0.033(1)
C(10)	0.6035(3)	0.6009(3)	0.2571(2)	0.029(1)
C(11)	0.7211(3)	0.5410(3)	0.2683(3)	0.041(1)
C(12)	0.7315(4)	0.4637(3)	0.3407(3)	0.048(1)
C(13)	0.6215(4)	0.4427(3)	0.3973(2)	0.044(1)
C(14)	0.5042(4)	0.5020(3)	0.3814(2)	0.036(1)
C(15)	0.2548(3)	0.9419(3)	0.2974(2)	0.034(1)
C(16)	0.4088(3)	0.9625(3)	0.3379(2)	0.029(1)
C(17)	0.4814(4)	1.0827(3)	0.3696(2)	0.038(1)
C(18)	0.6188(4)	1.0948(3)	0.4144(2)	0.043(1)
C(19)	0.6786(3)	0.9869(3)	0.4259(2)	0.039(1)
C(20)	0.6012(3)	0.8701(3)	0.3920(2)	0.033(1)
C(21)	0.0532(3)	0.7738(3)	0.2362(2)	0.030(1)
C(22)	−0.0399(3)	0.8585(3)	0.1900(2)	0.030(1)
C(23)	−0.0902(3)	0.9535(3)	0.2401(2)	0.036(1)
C(24)	−0.1787(4)	1.0252(3)	0.1938(3)	0.044(1)
C(25)	−0.2129(4)	0.9994(3)	0.1002(3)	0.048(1)
C(26)	−0.1570(4)	0.9042(4)	0.0559(3)	0.047(1)
Cl(1)	−0.5133(1)	1.2438(1)	0.1263(1)	0.043(1)
O(2)	−0.3599(4)	1.2731(4)	0.1342(4)	0.119(2)
O(3)	−0.5703(5)	1.2943(4)	0.2036(2)	0.098(1)
O(4)	−0.5635(4)	1.3039(3)	0.0477(2)	0.070(1)
O(5)	−0.5555(4)	1.1117(3)	0.1077(3)	0.096(1)
Cl(2)	0.0638(1)	0.2437(1)	0.4694(1)	0.052(1)
O(6A)	0.0623(15)	0.2134(17)	0.5601(7)	0.115(5)
O(7A)	0.1908(16)	0.3201(17)	0.4697(13)	0.189(9)
O(8A)	−0.0422(12)	0.2818(15)	0.4201(11)	0.142(8)
O(9A)	0.0894(13)	0.1267(9)	0.4217(7)	0.144(5)
O(6B)	0.0044(19)	0.1676(21)	0.5347(11)	0.135(7)
O(7B)	0.2037(12)	0.2734(18)	0.4515(11)	0.123(7)
O(8B)	−0.0329(18)	0.2125(18)	0.3964(9)	0.149(9)
O(9B)	0.0275(15)	0.3697(11)	0.5017(13)	0.176(8)

the water molecule were refined isotropically, and hydrogen atoms of the ligands were kept fixed in calculated positions with $d_{C-H}=0.95$ Å.

[Cr(tpen)](ClO$_4$)$_3$. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with four molecules in the unit cell. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in fixed calculated positions with $d_{C-H}=0.96$ Å. The perchlorate anion centred on Cl(2) is disordered around the Cl(2)–O(5) bond, with the remaining oxygen atoms each located in two sites with site occupation factors of 0.302 and 0.698, respectively. The anion centred on Cl(3) is similarly disordered around Cl(3)–O(9) with site occupation factors of 0.41 and 0.59 respectively.

[Cr(tpen)(OH)](ClO$_4$)$_2$. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with two molecules in the unit cell. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in fixed calculated positions with $d_{C-H}=0.96$ Å, except for the hydroxide ligand hydrogen atom attached to O(1), which was located in a Fourier map and refined isotropically. The oxygen atoms associated with the perchlorate anion centred on Cl(2) are each disordered between two sites with site occupation factors of 0.536 and 0.464.

Table 6. Fractional atomic coordinates and equivalent isotropic displacement parameters for *cis*-[Cr(tpen)$(OH)_2$]$(ClO_4)\cdot 3H_2O$ (**4**).

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Cr	0.05385(3)	0.10084(2)	0.06012(2)	0.0271(1)
Cl	0.12396(7)	−0.29749(5)	0.10967(4)	0.0549(4)
O(1)	0.1954(2)	0.1753(1)	0.0323(1)	0.046(1)
O(2)	−0.0727(2)	0.1172(1)	−0.0134(1)	0.043(1)
N(1)	−0.0680(2)	−0.0029(1)	0.0973(1)	0.028(1)
N(2)	0.1442(2)	0.0029(1)	0.0081(1)	0.035(1)
N(3)	−0.2934(2)	−0.0845(1)	0.2002(1)	0.045(1)
N(4)	0.1607(2)	0.0846(1)	0.1574(1)	0.028(1)
N(5)	−0.0392(2)	0.1908(1)	0.1201(1)	0.030(1)
N(6)	0.3704(2)	−0.0038(1)	0.2622(1)	0.049(1)
C(1)	0.0127(2)	−0.0391(1)	0.1558(1)	0.030(1)
C(2)	0.0702(2)	0.0295(1)	0.2003(1)	0.031(1)
C(3)	−0.0733(2)	−0.0619(1)	0.0387(1)	0.037(1)
C(4)	0.0655(2)	−0.0660(1)	0.0038(1)	0.036(1)
C(5)	0.1099(3)	−0.1350(2)	−0.0327(1)	0.052(2)
C(6)	0.2346(3)	−0.1326(2)	−0.0661(2)	0.063(2)
C(7)	0.3139(3)	−0.0618(2)	−0.0633(2)	0.059(2)
C(8)	0.2669(2)	0.0051(2)	−0.0254(1)	0.045(1)
C(9)	−0.2133(2)	0.0205(1)	0.1196(1)	0.032(1)
C(10)	−0.3065(2)	−0.0516(1)	0.1371(1)	0.036(1)
C(11)	−0.4034(2)	−0.0800(2)	0.0899(1)	0.049(1)
C(12)	−0.4907(3)	−0.1444(2)	0.1074(2)	0.066(2)
C(13)	−0.4764(3)	−0.1791(2)	0.1712(2)	0.073(2)
C(14)	−0.3777(3)	−0.1476(2)	0.2152(2)	0.065(2)
C(15)	0.1679(2)	0.1685(1)	0.1881(1)	0.038(1)
C(16)	0.0318(2)	0.2137(1)	0.1768(1)	0.033(1)
C(17)	−0.0160(3)	0.2757(2)	0.2191(1)	0.050(1)
C(18)	−0.1388(3)	0.3152(2)	0.2041(2)	0.055(2)
C(19)	−0.2114(3)	0.2919(2)	0.1465(1)	0.050(1)
C(20)	−0.1591(2)	0.2295(1)	0.1058(1)	0.040(1)
C(21)	0.3043(2)	0.0481(1)	0.1493(1)	0.034(1)
C(22)	0.3953(2)	0.0520(1)	0.2125(1)	0.037(1)
C(23)	0.5019(3)	0.1098(2)	0.2160(1)	0.049(1)
C(24)	0.5865(3)	0.1101(2)	0.2731(2)	0.063(2)
C(25)	0.5616(3)	0.0545(2)	0.3246(1)	0.068(2)
C(26)	0.4535(3)	−0.0006(2)	0.3173(1)	0.062(2)
O(3)	0.0914(3)	−0.3584(1)	0.1617(1)	0.082(2)
O(4)	0.0006(3)	−0.2571(2)	0.0927(2)	0.102(3)
O(5)	0.2125(3)	−0.2377(2)	0.1374(1)	0.101(2)
O(6)	0.1810(6)	−0.3350(2)	0.0543(2)	0.176(4)
O(7)	0.1246(2)	−0.5385(1)	0.1734(1)	0.065(1)
O(8)	0.4774(2)	0.2007(2)	0.0523(1)	0.077(2)
O(9)	−0.3472(3)	0.1213(3)	−0.0432(2)	0.107(2)

cis-*[Cr(tpen)$(OH)_2$]$(ClO_4)\cdot 3H_2O$.* The complex crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$with four molecules in the unit cell. All non-hydrogen atoms were refined anisotropically; coordinates of the hydrogen atoms of the hydroxide ligands and of the water molecules were refined isotropically. Hydrogen atoms of the tpen ligand were kept fixed in calculated positions with $d_{C-H}=0.95$ Å. The Rogers factor[14] was −0.90(3).

Analyses, spectra and kinetics measurements. Microanalyses were performed by the analytical sections of the Chemical Institute at the University of Copenhagen. Absorption spectra were measured on Perkin-Elmer Lambda 17 and Lambda 18 UV/VIS spectrophotometers equipped with Perkin-Elmer digital temperature controllers. Stopped-flow kinetics measurements were made on an Applied Photophysics SX.18MV Stopped-flow spectrometer.

Methods of calculation. All parameter values were determined by minimizations within the framework of non-linear regression analysis. The method used to determine the acid dissociation constants[15,16] and rate constants for kinetic runs followed at a single wavelength[17] has been described previously. The parameters in Scheme 1 were calculated by simultaneous minimization of all rate and equilibrium data as a function of the relevant parameters.

Acknowledgments. The Applied Photophysics SX.18MV stopped-flow spectrometer was obtained by a grant from *Statens naturvidenskabelige Forskningsråd* to

J. Springborg. A.H. is indebted to the Carslberg Foundation for the diffractometers. This research has been supported by *Statens naturvidenskabelige Forskningsråd* through grant J.nr.11-7783.

References

1. Håkansson, K., Carlsson, M., Svensson, L. A. and Liljas, A. *J. Mol. Biol. 227* (1992) 1192.
2. Merz, K. M. *J. Mol. Biol. 214* (1990) 799.
3. Eriksson, A. E., Jones, T. A. and Liljas, A. *Proteins 4* (1988) 274.
4. Eriksson, A. E., Jones, T. A. and Liljas, A. In Bertini, L., Luchinat, C., Maret, W. and Zeppezauer, M., Eds. *Zinc Enzymes.* Birkhäuser. Boston 1986. p. 317.
5. Toftlund, H., Simonsen, O. and Pedersen, E. *Acta Chem. Scand. 44* (1990) 676.
6. Toftlund, H. and Yde-Andersen, S. *Acta Chem. Scand., Ser. A 35 (1981) 575.*
7. *Burnett, M. N. and Johnson, C. K. ORTEP III.* Report ORNL-6895. Oak Ridge National Laboratory, Oak Ridge, TN 1996.
8. Results will be published soon.
9. Siemens. *SMART* Area -Detector Control and Integration Software. Siemens Analytical X-Ray Insts. Inc. Madison, WI 1995.
10. Sheldrick, G. M. *SHELXTL Crystallographic System,* Versions 4.2 and 5.03/Iris, Siemens Analytical X-Ray Insts. Inc., Madison, WI 1991, 1994.
11. Hazell, A. *KRYSTAL* An Integrated System of Crystallographic Programs. Aarhus University, Denmark 1995.
12. *International Tables for X-Ray Crystallography.* Kynoch Press, Birmingham 1974, Vol. IV (present distributor, Kluwer, Dordrecht).
13. *International Tables for Crystallography.* Kluwer, Dordrecht 1992, Vol. C.
14. Rogers, D. *Acta Crystallogr., Sect. A 37* (1981) 734.
15. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 30* (1978) 203.
16. Mønsted, O. and Skibsted, L. H. *Acta Chem. Scand., Ser. A 38* (1984) 23
17. Eriksen, J., Mønsted, L. and Mønsted, O. *Acta Chem. Scand. 46* (1992) 521.

Received March 18, 1999.