(weight loss found 26.7 %, theor. 27.1 %). No change in weight was recorded between 400 and 760°C; corresponding to the formula $ZnSO_4$. Above that, the formation of a basic zinc(II) sulphate began.[8] The temperature ranges within which the thermal decompositions occur are almost the same in nitrogen and air.

The infrared spectrum of $ZnLSO_4.3H_2O$ supports the view that the water molecules are not structural water, for there is no band indicating coordination of water in the spectrum.[9] All vibrations, ν_1, ν_2, ν_3, ν_4, of the sulphate group seem to be infrared active. The bands appear in the following regions: ν_1 975, 980 cm^{-1} (m), ν_2 440 cm^{-1} (m), ν_3 1050 – 1070, 1105, 1130 – 1160 cm^{-1} (vs), and ν_4 560 (m), 610(s), 670 cm^{-1} (m). These bands are in very good agreement with the data reported by Nakamoto and co-workers[10] and Eskenazi *et al.*[11] and consistent with the presence of a C_{2v} bridging sulphato group. Assignments are a little difficult because the ν_1 and ν_3 bands overlap with those of the ligand.

Because the sulphate group acts as a bidentate ligand and the water molecules in all probability are not coordinated, the only possibility is that the pyrazine is bridge forming, the bands at 975 and 980 cm^{-1} are due only to the sulphate group and the coordination around the zinc atom is tetrahedral.

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Received May 10, 1972.

Structural Studies on the Rare Earth Carboxylates. 15. The Unit Cell Dimensions of the Isostructural Series Tri-Aquo Iminodiacetato Lanthanoid(III) Chloride

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Prutkova *et al.* have reported preparation methods and IR spectra for a series of compounds with the composition $M(OCOCH_2NHCH_2OCO)Cl.nH_2O$, M = Pr – Lu and $n = 2$ or 3.[1] In a systematic study of rare earth oxydiacetate,[2,3] iminodiacetate, [4,5] and thiodiacetate [6] compounds at this institute, the structure of tri-aquo iminodiacetato neodymium(III) chloride, denoted NIC below, has previously been determined.[5]

The crystal radius of the trivalent ions is monotonously decreasing in the lanthanoid series.[7–9] The aim of the present investigation is to establish if the lanthanoid contraction causes any phase transformations within the series of the iminodiacetate compounds and, if not, to study the correlation between the lattice parameters and the lanthanoid contraction.

Compounds with the composition $M(C_4H_5O_4N)(H_2O)_3Cl$, M = Pr – Lu, were prepared and analysed as described previously for NIC.[5] Powder photographs were taken as described elsewhere.[3] All the compounds gave the same powder pattern as NIC, thus crystallizing in the orthorhombic space group $P2_12_12_1$. The reflexions were indexed using approximate unit cell dimensions obtained in the single crystal investigation of NIC. The lattice parameters were then improved as described in Ref. 3.

Table 1 gives the lattice parameters and the unit cell volumes, V, with their estimated standard deviations. A table comparing the observed and calculated values of $\sin^2\theta$ for the investigated compounds may be obtained on request from the author. The lattice parameters and $V^{1/3}$ are plotted in Fig. 1 *versus* the crystal radii, r, for six-coordination as determined by Templeton and Dauben.[9] A justification for the use of this set of ionic radii is given in Ref. 10. All quantities, except c, are

Table 1. The lattice parameters and unit cell volumes with estimated standard deviations.

M	a/Å	b/Å	c/Å	V/Å^3
Pr	8.3934(23)	14.2438(43)	8.4713(25)	1012.8(5)
Nd	8.3565(12)	14.1632(24)	8.4243(13)	997.1(3)
Sm	8.3271(30)	14.1146(43)	8.4043(27)	987.8(6)
Eu	8.2865(49)	14.0816(93)	8.3746(36)	977.2(10)
Gd	8.2840(29)	14.0630(54)	8.3783(29)	976.1(6)
Tb	8.2616(37)	14.0153(61)	8.3526(37)	967.1(7)
Dy	8.2339(34)	13.9648(74)	8.3516(35)	960.3(8)
Ho	8.2160(25)	13.9521(45)	8.3359(32)	955.6(6)
Er	8.1919(27)	13.9224(42)	8.3219(28)	949.1(5)
Tm	8.1891(24)	13.9034(44)	8.3234(21)	947.7(5)
Yb	8.1729(21)	13.8808(36)	8.3318(25)	945.2(4)
Lu	8.1255(26)	13.8297(39)	8.2909(19)	931.7(5)

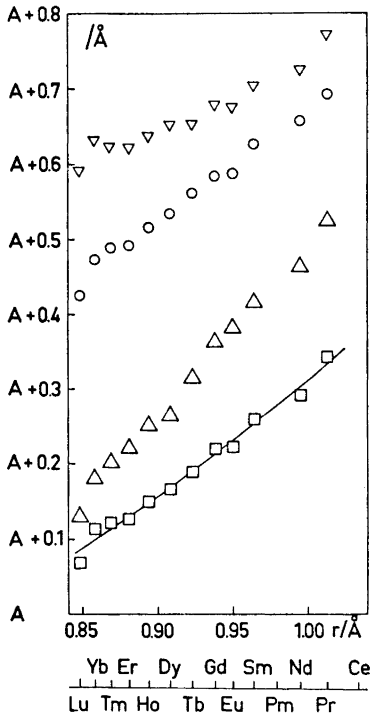

Fig. 1. The unit cell dimensions and $V^{1/3}$ plotted *versus* the crystal radius r of the trivalent lanthanoid ions. The symbols refer to a (○), b (△), c (▽) and $V^{1/3}$ (□), and A has the values 7.7, 13.7, 7.7, and 9.7, respectively.

monotonously increasing functions of r. The coordination polyhedra in NIC form infinite chains in the c direction by sharing the carboxylate oxygen atoms O(1).[5] Since the geometry of the coordination polyhedron might vary through the series, a changed position of O(1) could in some cases increase the parameter c with decreasing ionic radius. The smaller over-all effect of the lanthanoid contraction on parameter c as compared to a and b supports this view. Information on these matters cannot be obtained without knowledge of the detailed structure of at least one more compound besides NIC. For the same reason, the influence of van der Waals repulsion and hydrogen bonding on the lattice parameters as discussed by Albertsson [3,11] and Grenthe,[12] cannot be elucidated.

The preparation method used gives a cerium compound crystallizing in the orthorhombic system but with a unit cell volume of 1480 Å^3, considerably larger than expected for a cerium compound isostructural with NIC.

This work is part of a research project supported by the *Swedish Natural Science Research Council.*

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Received May 4, 1972.

The Rate of Formation of the Enzyme-Substrate Compound I between Hydroxymethylhydroperoxide and Horseradish Peroxidase

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Hydroxymethylhydroperoxide, $HOCH_2OOH$ (HMP) is a peroxide substrate and a rapid irreversible inhibitor of horseradish peroxidase.[1]* A direct determination of the rate constant (k_1) for the formation of the enzyme-substrate compound I[2] from peroxidase and HMP has been precluded by the obligate presence of H_2O_2 in HMP-preparations; an indirect method gave $k_1 \simeq 2 \times 10^5$ M^{-1} sec^{-1}. However, at a study of the effects of HMP on catalase it was found that the enzyme could remove H_2O_2 from aqueous HMP solutions.[4] The present paper reports a stopped-flow determination of the rate constant (k_1) for the formation of the enzyme-substrate compound I from HMP and peroxidase.

H_2O_2, HCHO, HMP, and bis(hydroxymethyl)peroxide, $HOCH_2OOCH_2OH$ (BHMP) form an equilibrium in water solution.[3] The equilibrium is catalyzed by H^+ and OH^-, predominantly by the latter at pH > 3.[3] At the conditions of the present experiments (pH 4.25, 25°C), HMP and BHMP are rather stable, the half-times of their hydrolyses being longer than 12 and 5 h, respectively.[3]

Results and discussion. Catalase was used to remove H_2O_2 from HMP solutions. The enzyme is partially transferred to the inactive[8] compound II by HMP,[4] but there is always some active catalase left to remove H_2O_2 from HMP solutions, as seen in Fig. 1.

The HMP solutions to be used in the stopped-flow experiments contained 5 times more catalase than was used in the experiment of Fig. 1. HMP was dissolved ($\simeq$ 0.45 mM) in 10 mM sodium acetate, pH 4.25, 0°, with 35 nM catalase ("stock solution"). After 20 min the H_2O_2 content was assumed to be low enough and a sample was diluted with 4, 9, or 19 volumes of the same buffer at 25°. These solutions were left to equilibrate for 10 min and then used in the stopped-flow apparatus. The content of HMP of the "stock solution" was repeatedly assayed by means of peroxidase and guaiacol.[1]

The stopped-flow runs (Fig. 2) gave an average k_1 of 5×10^5 M^{-1} sec^{-1} k_1 has previously been determined to 2×10^5 M^{-1} sec^{-1} by an indirect method in the presence of 6.7 mM guaiacol.[1] A part of this discrepancy may be explained by the blocking effect of hydrogen donor substrates on peroxidase (Ref. 9 and S. Marklund, unpublished experiments) at this rather high concentration. The previous investigation[1] was also performed with higher HMP-concentrations (50 – 90 μM) than the present (6.8 – 38.9 μM, Fig. 2) in which the observed k_1-values may show a tendency to decrease with increasing HMP concentration.

The higher k_1 of the present experiments cannot be due to interference from H_2O_2 still present in the catalase-treated HMP solutions. In the experiment with 6.8 μM HMP in Fig. 2, the presence of 0.23 μM H_2O_2 ($k_1 = 9 \times 10^6$ M^{-1} sec^{-1}, Ref. 2) would

* Horseradish peroxidase, Donor: Hydrogen peroxide oxidoreductase, E.C. 1.11.1.7; Catalase, Hydrogen peroxide : Hydrogen peroxide oxidoreductase, E.C. 1.11.1.6.