

Short Communications

Studies on Metal Complexes of Pyrazine and Its Derivatives. Part XI. Crystal Data and Other Properties of Mono(pyrazine)zinc(II) Sulphate Trihydrate

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Pyrazine and other diazines (pyrimidine and pyridazine) form complexes with divalent metals where the molar ratio is either 1 : 1 or 1 : 2.¹⁻³ It seems, however, that the molar ratio of azine to zinc(II) is 1 : 1 in most zinc(II)-azine complexes; only pyridazine forms a 1 : 2 complex.^{4,5} All the complexes referred to above are either halide or pseudohalide compounds. In a previous paper³ the formation of a 1 : 1 adduct by pyrazine and zinc(II) chloride and bromide was reported. Crystal data and other properties of mono(pyrazine)zinc(II) sulphate trihydrate are presented in this paper.

Preparation and analysis. Pyrazine of *puriss.* grade from Koch-Light Laboratories, Ltd., was used without purification. The other chemicals used were analytical reagents.

Mono(pyrazine)zinc(II) sulphate trihydrate, $\text{ZnLSO}_4 \cdot 3\text{H}_2\text{O}$, precipitated when a methanolic solution of zinc(II) sulphate heptahydrate (20 mmol) was added dropwise to a methanolic solution of pyrazine (40 mmol). The salt was washed with ethanol and ether and recrystallised from ethanol containing 15 % water. (Found: Zn 22.2; C 16.3; N 9.4; O 37.7. Calc. for $\text{ZnLSO}_4 \cdot 3\text{H}_2\text{O}$: Zn 22.1; C 16.3; N 9.5; O 37.9.)

Measurements. The thermogravimetric curves were recorded on a Perkin-Elmer Thermobalance TGS-I at a heating rate of 20°/min. The sample weighed about 1 mg. The thermal decomposition was carried out in nitrogen

and in air over a range of temperature from 27 to 800°C. The other apparatuses and methods have been described in earlier papers of this series.^{6,7}

Results and discussion. Mono(pyrazine)zinc(II) sulphate trihydrate, $\text{ZnLSO}_4 \cdot 3\text{H}_2\text{O}$, was found to be triclinic and the space group is thus $P1$ or $P\bar{1}$. The powder photographs were indexed using approximate unit cell dimensions estimated from rotation and Weissenberg photographs. More accurate values of the unit cell dimensions were obtained from the uniquely indexed reflections by a least squares fit. The density as determined by flotation in carbon tetrachloride-methyl iodide mixtures is 1.83 g cm⁻³ and the calculated density on the basis of a unit cell containing one formula unit of $\text{ZnLSO}_4 \cdot 3\text{H}_2\text{O}$ is 1.81 g cm⁻³. The crystal data are collected in Table 1.

Table 1. Crystal data for mono(pyrazine)zinc(II) sulphate trihydrate.

$a = 10.734 \pm 0.002 \text{ \AA}$	$V = 271 \text{ \AA}^3$
$b = 4.427 \pm 0.001 \text{ \AA}$	$D_{\text{obsd}} = 1.83 \text{ g cm}^{-3}$
$c = 6.927 \pm 0.002 \text{ \AA}$	$D_{\text{calcd}} = 1.81 \text{ g cm}^{-3}$
$\alpha = 121.15 \pm 0.03^\circ$	F.W. = 295.60
$\beta = 82.57 \pm 0.02^\circ$	$Z = 1$
$\gamma = 104.02 \pm 0.03^\circ$	

The thermogravimetric curve shows that the three molecules of water of $\text{ZnLSO}_4 \cdot 3\text{H}_2\text{O}$ were removed rapidly at 115°C. At 155°C the thermolysis curve leveled off at a weight corresponding to the composition of the anhydrous salt ZnLSO_4 (weight loss found 18.7 %, theor. 18.3 %). The water molecules are thus quite easily removed and probably are not structural water. The deamination occurs in two steps between 280 and 400°C, rapidly at first but then more slowly

(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 $\text{ZnLSO}_4 \cdot 3\text{H}_2\text{O}$ 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-workers¹⁰ and Eskenazi *et al.*¹¹ and consistent with the presence of a C_{2v} bridging sulphate group. Assignments are a little difficult because the ν_1 and ν_2 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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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 $\text{M}(\text{OCOCH}_2\text{NHCH}_2\text{OCO})\text{Cl} \cdot n\text{H}_2\text{O}$, $\text{M} = \text{Pr} - \text{Lu}$ and $n = 2$ or 3 .¹ In a systematic study of rare earth oxydiacetate,^{2,3} iminodiacetate,^{4,5} and thiodiacetate⁶ 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 $\text{M}(\text{C}_4\text{H}_7\text{O}_4\text{N})(\text{H}_2\text{O})_3\text{Cl}$, $\text{M} = \text{Pr} - \text{Lu}$, 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 I 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