LETTERS TO THE EDITOR

THE CRYSTAL STRUCTURE OF MANGANESE MALONATE DIHYDRATE $C_3H_2O_4 \cdot Mn, 2H_2O$

THE title compound was investigated to unravel the scheme of hydrogen bonds as well as to study the oxygen ligands around the manganese.

Synthesis.—The crystals of manganese malonate dihydrate were prepared by taking malonic acid and manganese carbonate in the ratio of 2 : 1; water being used as solvent. The concentrated solution was left for slow evaporation till needle-shaped crystals began to appear. The mother liquor was removed by decantation and the crystals were washed with alcohol and acetone.

Crystal data.—Orthorhombic with $a = 9{\cdot}55$, $b = 7{\cdot}40$, $c = 8{\cdot}37$ Å. $D_{calc} = 2{\cdot}17$, $D_{obs.} = 2{\cdot}14$ gm/cc, $Z = 4$. Space group absences could lead to $Pca2_1$ or Pcam. As there are only four formula units in the unit cell with the malonate residue unlikely to possess a mirror symmetry, space group $Pca2_1$ was assumed which has been confirmed by structure determination. Reflexions (460) were collected photographically using Weissenberg photography and intensities estimated visually. Usual corrections were applied and the data brought to absolute scale by statistical methods.

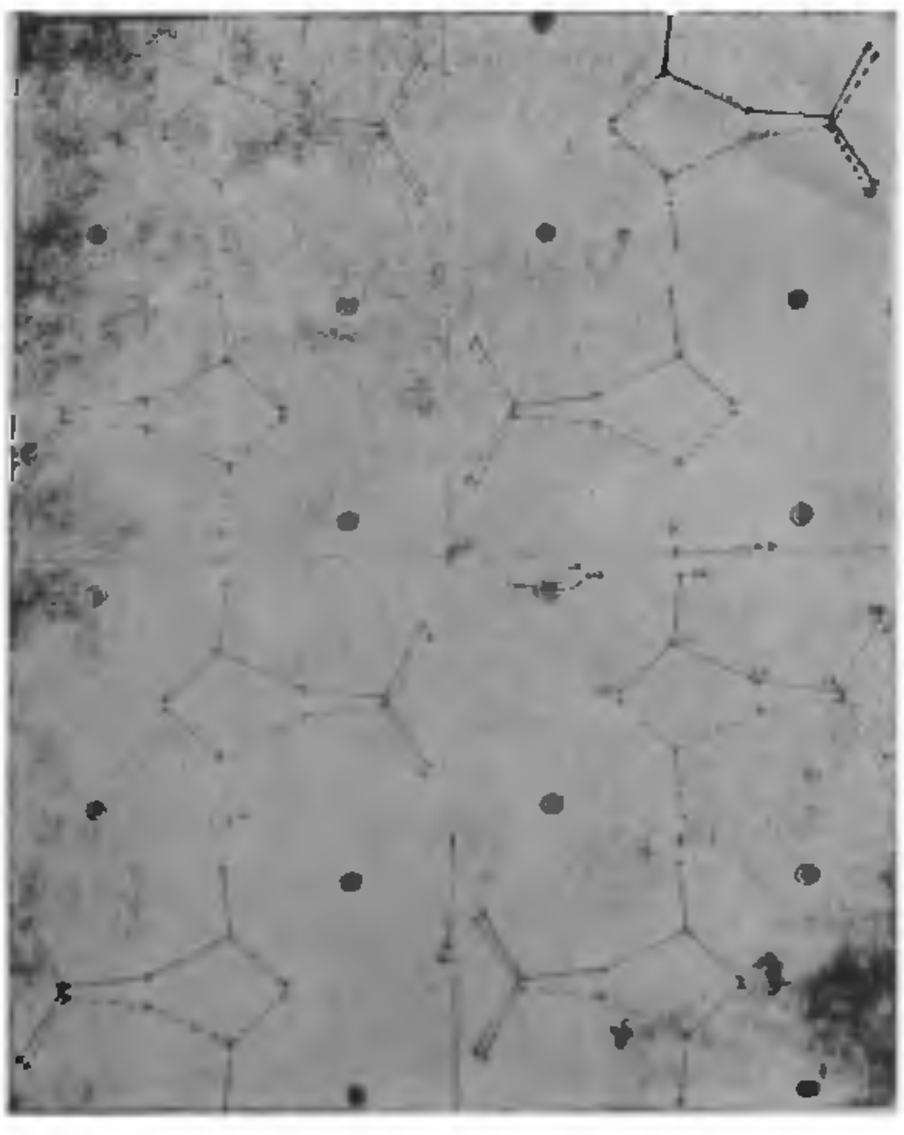

FIG. 1. Crystal structure looking down [001].

Crystal structure and comments.—The heavy atom was located from three-dimensional Patterson synthesis. The projection down the [001], being centrosymmetric, was solved by phasing the reflexions from heavy atom contribution. [001] Fourier was refined by series of successive syntheses. The z-coordinates were roughly located from packing considerations and adjusted by trial and error methods. At the present stage of analysis (with only overall isotropic temperature factor) R (hkO) $= 0{\cdot}16$, R (Okl) $= 0{\cdot}17$, R (hkl) $= 0{\cdot}18$.

A view of the structure down [001] is shown in Fig. 1. In the crystal, manganese is six-fold co-ordinated with Mn–O distances ranging from 2·08 Å to 2·22 Å. The water molecules and the surrounding oxygen atoms form a distorted octahedron. There are several short contacts between the oxygen atoms ranging from 2·82 Å to 3·20 Å, some of which may be short contacts between oxygen atoms of the polyhedra and some hydrogen bonds. As considerable interest lies in deciding the scheme of hydrogen bonds in the crystal, further least-squares refinement of the data is in progress.

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SALICYLIC ACID AND RELATED COMPOUNDS AS INDICATORS FOR THE DIRECT N-HYDROXY ETHYL ETHYLENE DIAMINE TRIACETIC ACID (HEDTA) TITRATION OF FERRIC IONS

No indicators have been reported for the direct titration of N-hydroxy ethyl ethylene diamine triacetic acid (HEDTA) with ferric ions. The present article reports the use of salicylic acid, sulphosalicylic acid and salicylamide as indicators for the direct HEDTA titration of ferric ions. All the three substances give violet colours with ferric ions. When such a solution was titrated with HEDTA the characteristic violet colour gave place to yellow at the end point.

Materials

Aqueous ferric nitrate solution (0·1 M) and HEDTA solution (2·78 g/l) were employed in this work. Indicator solution had 1 g indicator in 100 cc alcohol. The solution was stable for four weeks. Metal solutions had a concentration of 0·2 M.

Suggested Procedure

The ferric nitrate solution (5 ml of 0·01 M) is brought to pH 1·0 by adding dil. nitric acid and this is mixed with four drops of a 1% solution of the indicator and suitably diluted and titrated against standard HEDTA solution to a deep yellow colour. The results are compared with EDTA titrations. Good values are obtained in the pH range of 1–3.

Effect of Ferric Ion Concentration

Accurate results (error < ·5%) were obtained with 1·0 ml of the ferric nitrate solution in the concentration range from 0·01 M to 0·001 M. Thus micro titration of ferric ions with HEDTA is feasible with these indicators.

Effect of Foreign Ions

Synthetic solutions containing 2·8 mg iron (III) were titrated at pH 1·0. It was found that 100 fold excess of Na^+, K^+, NH_4^+, La^{3+}, Cs^+, Be^{2+}, UO_2^{2+}, Cl^- Br^-, NO_3^- and SO_4^{2-}, 4 fold excess of Ca^{2+}, Ba^{2+} and Sr^{2+}, 2-fold excess of Zn^{2+}, Mg^{2+}, Al^{3+}, Mn^{2+}, Cd^{2+} Cu^{2+}, Ni^{2+}, Co^{2+} an equal amount of Pb^{2+}, Ag^+, Cr^{3+} and HCO_3^- could be tolerated (*i.e.*, error < 1%). The tolerance was increased to five times by masking in the case of Cu^{2+} by thiosulphate, in the case of Mn^{2+} by hydrogen peroxide and in the case of Zn^{2+} by glycerine. Phosphate, fluoride, oxalate, vanadate, molybdate and tungstate interfered at all levels.

Applications

The above procedure was applied to the determination of ferric ions in the analysis of pharmaceuticals containing iron in the form of colloidal iron hydroxide ferrous gluconate, ferrous fumarate, and ferrous sulphate (Table I). The bauxite ore was analysed by the suggested procedure. The expected iron content was 2·86% Fe_2O_3 while that found by the above procedure was 2·80% Fe_2O_3.

TABLE I

Analysis of drugs containing iron by direct titration with HEDTA

Name of drug	Fe^{3+} expected (g)	Fe^{3+} found (g)		
		Salicylic acid	Salicylamide	Sulphosalicylic acid
Polycytol tablet (ferrous sulphate)	0·195	0·194	0·194	0·194
Iberol tablet (do.)	0·525	0·524	0·522	0·522
Iberol liquid (do.)	0·131	0·130	0·130	0·130
Livogen capsule (ferrous fumarate)	0·150	0·145	0·149	0·147
Microfer tablet (ferrous gluconate)	0·195	0·194	0·194	0·194
Tonoferon drops (ferric hydroxide)	0·050	0·047	0·046	0·046

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THERMAL DECOMPOSITION OF ZINC AND CADMIUM HEXAOXOIODATES

Introduction

Several reports have been published on the thermal decomposition of the lanthanide and other group III hexaoxoiodates[1–4]. However, there appears to be no data available in the literature concerning the thermal decomposition of zinc and cadmium hexaoxoiodate (VII). The purpose of this work is to study the thermal decomposition of the above-mentioned periodates by means of thermogravimetric and differential thermal analysis.

Experimental

Zinc and cadmium hexaoxoiodates (VII) ($M_2HIO_6 \cdot 1{\cdot}25\ H_2O$, where M = Zn, Cd) were prepared by mixing in stoichiometric proportion, equimolar dilute solutions of the reagent grade periodic acid and the respective metal acetates, followed by filtration and drying in a vacuum desiccator over P_2O_5. The dried and powdered compounds were chemically analysed for metal, iodine and water contents. Metal ions were analysed complexometrically. Iodine was analysed gravimetrically as AgI and water was determined by Karl Fischer method. The analytical results are given in Table I.

Differential thermal analysis of both periodates was carried out using 'Stanton Thermoanalyser' with a programmed heating rate of 10°C/min., in an air atmosphere with sample weights of 175 to 200 mg. The sample holder was a cylindrical platinum crucible and α-alumina served as a reference material. Thermogravimetric analysis of the compounds were carried out in air in a 'Stanton Mass Flow Thermobalance' with a programmed heating rate of 2° C/min. with sample weights ~ 500 mg.

Results and Discussions

Figure 1 shows the thermogravimetric and DTA curves of zinc and cadmium hexaoxoiodate hydrates ($M_2HIO_6 \cdot 1{\cdot}25\ H_2O$). It is evident from the TG curves that the first weight loss begins at 60° C and terminates at 210° C for zinc and at 275° C for cadmium hexaoxoiodate hydrate respectively. This weight loss