

- BATTINO, R., *Chem. Rev.*, **71** (1971), 5.
- DESHPANDE, D. D. & OSWAL, S. L., *J. chem. Soc. Faraday Trans. I.*, **68** (1972), 1059.
- DESHPANDE, D. D. & OSWAL, S. L., *J. chem. Thermodyn.*, **7** (1975), 155.
- TIMMERMANS, J., *Physico-chemical constants of pure organic compounds* (Elsevier), 1965.
- DIAZ-PENA, M. & MCGLASHAN, M. L., *Trans. Faraday Soc.*, **57** (1961), 1511.
- DESHPANDE, D. D. & BHATGADDE, L. G., *J. phys. Chem.*, **72** (1968), 261.
- DESHPANDE, D. D., BHATGADDE, L. G., OSWAL, S. L. & PRABHU, C. S., *J. chem. Engng Data*, **16** (1971), 469.
- GUGGENHEIM, E. A., *Mixtures* (Oxford University Press, London), 1952.
- DESHPANDE, D. D. & PRABHU, C. S., *Indian J. Chem.*, **16A** (1978), 95.
- ANDREWS, A. W. & MORKOM, K. W., *J. chem. Thermodyn.*, **3** (1971), 513.
- ARM, H. & BANKAY, D., *Helv. chim. Acta*, **52** (1969), 279.
- ERVA, J., *Suomen Kemi.*, **28B** (1955), 131.
- DINCER, S. & VAN NESS, H. C., *J. chem. Engng data*, **16** (1971), 378.
- MCKINNON, I. R. & WILLIAMSON, A. G., *Aust. J. Chem.*, **17** (1971), 1374.

Thermal Behaviour of Silver Chlorate

M. R. UDUPA

Department of Chemistry, Indian Institute of Technology,
Madras 600 036

Received 2 February 1979; accepted 16 March 1979

The thermal decomposition of silver chlorate has been followed by TG, DTA, IR spectroscopy and X-ray powder diffraction studies. The results suggest that a part of silver chlorate gets oxidized to silver perchlorate during the decomposition and the final product is found to be silver chloride.

Thermal behaviour of alkali metal chlorates revealed that they were congruently melting and decomposed to metal chlorides¹⁻³. During decomposition, a part of the chlorates underwent disproportionation to perchlorates and chlorides¹⁻³. Recently we have studied the thermal behaviour of TlClO_3 (ref. 4) and KClO_3 (ref. 5). Silver(I) resembles alkali metals and thallium(I) in some of its crystallo-chemical behaviour. It is therefore, interesting to study the thermal behaviour of silver chlorate and compare it with that of alkali metal and thallium(I) chlorates. The decomposition studies are followed by TG, DTA, IR spectral measurements and X-ray powder diffraction patterns.

Silver(I) chlorate was prepared by mixing equal volumes of aqueous solutions containing equimolar ratios of silver sulphate and barium chlorate. The precipitated BaSO_4 was filtered and the clear solution evaporated on a water-bath. AgClO_3 , thus obtained had d_{hkl} values (Å), 2.90s, 3.01m, 3.43m, 4.25m, which agreed⁶ with the reported values.

The TG studies were made in air using Stanton recording thermobalance and DTA in air on a Netzsch differential thermal analyzer. The X-ray powder diffraction patterns were taken with a Debye-Scherrer

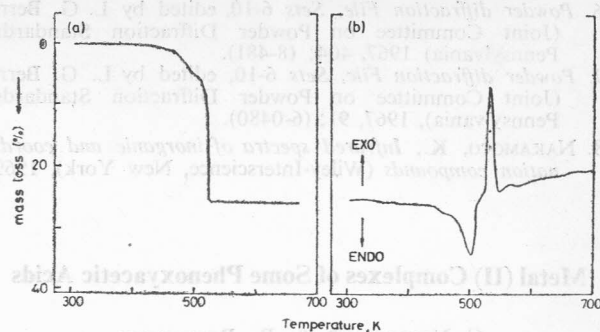


Fig. 1 — TG plot (a) and DTA plot (b) of AgClO_3

camera of 0.1146m diam., using $\text{CuK}\alpha$ radiation. The IR spectra were recorded in KBr in the range 1400–600 cm^{-1} on a Perkin Elmer 257 spectrometer.

The TG curve of AgClO_3 obtained by heating at 6°C min^{-1} is given in Fig. 1a and it indicates that the decomposition starts at 443K and is complete around 525K. The mass loss of 26%, observed from the TG curve (expected 25.1%) corresponds to the formation of AgCl . This is confirmed by the chemical analysis of silver content in the residue (Found : Ag, 74.6. Reqd : Ag, 75.3%). Further the X-ray powder patterns of the product gave the d_{hkl} values, 1.96 m 2.77s, 3.20s which agreed⁷ with those of AgCl . On close observation of the TG curve, it is apparent that there are two stages of decomposition, the first commencing at 443 and completing around 493K. The second stage overlaps on the first and completes by 525K.

In order to find out the intermediates of decomposition, a known amount of AgClO_3 was heated to 473K and when the reaction just initiated, the mixture was withdrawn from the furnace. The product was found to be fused and its IR spectrum was compared with those of free AgClO_4 and AgClO_3 . The partially decomposed AgClO_3 had absorptions ~ 1100 , characteristic of $\nu\text{Cl-O}$ of perchlorate and 970s, 945 cm^{-1} due $\nu\text{Cl-O}$ of chlorate⁸. This clearly suggests that during the decomposition a part of chlorate is oxidized to perchlorate ($\nu\text{Cl-O} \sim 1100 \text{ cm}^{-1}$), an observation similar to that found in the case of alkali metal and thallium(I) chlorates.

The DTA plot (Fig. 1b) suggests that the decomposition starts with an endothermic reaction at 493K which is immediately followed by an exothermic process at 523K. The endothermic effect may be attributed to the combined effect of fusion of AgClO_3 and formation of AgClO_4 which is followed by expulsion of oxygen in the exothermic effect to give AgCl as the final product.

References

- MARKOWITZ, M. M., BORYTA, D. A. & STEWART, H., *J. phys. Chem.*, **68** (1964), 2282.
- FREEMAN, E. S. & RUDLOFF, W. K., *Differential thermal analysis*, edited by R. C. Mackenzie (Academic Press, London), 1970, 364.
- SOLYMOSI, F. & BANSAGI, J., *Acta chim. Acad. Sci. Hung.*, **56** (1968), 357.
- UDUPA, M. R., *Thermochim. Acta*, **16**; 1976), 182.
- UDUPA, M. R., *Indian J. Chem.*, **15A** (1977), 556.

6. *Powder diffraction File, Sets 6-10*, edited by L. G. Berry (Joint Committee on Powder Diffraction Standards, Pennsylvania) 1967, 404; (8-481).
7. *Powder diffraction File, Sets 6-10*, edited by L. G. Berry (Joint Committee on Powder Diffraction Standards, Pennsylvania), 1967, 91; (6-0480).
8. NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (Wiley-Interscience, New York), 1969.

Metal (II) Complexes of Some Phenoxyacetic Acids

C. NATARAJAN* & R. RENGASAMY

Department of Chemistry, Madurai Kamaraj University,
Madurai 625 021

Received 8 November 1978; revised 5 February 1979;
accepted 3 April 1979

Manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II), lead(II) and UO_2^{2+} -phenoxyacetates and 4-x-phenoxyacetates (x = chloro, methyl and nitro group) of the type $\text{ML}_2 \cdot n\text{H}_2\text{O}$ have been isolated and characterized on the basis of elemental analyses, spectral, magnetic and thermal data. The magnetic moments and electronic spectra are consistent with octahedral geometry for all the complexes except copper which may have planar geometry. Curiously, *p*-methyl- and *p*-nitro-phenoxyacetates of Fe(II) show antiferromagnetic behaviour. IR spectra are indicative of symmetrical chelating acetate group in uranyl complexes and unidentate carboxylate group probably with the coordination of phenoxy-oxygen to copper in Cu(II) complexes. All the other complexes have been identified to contain bridging acetate groups. The shift in $\nu_{\text{as}}\text{COO}$ follows Irving-Williams order of stability of complexes with the exception of copper. $\Delta\nu$ is found to be affected by the phenyl substituents only in the case of Cu(II) complexes.

ALTHOUGH X-ray structure determinations have been made on a few metal(II) phenoxyacetates¹⁻³, no systematic investigation as to the nature of bonding and structure has been made using IR spectroscopy and other physical techniques. Phenoxyacetate ion is ambidentate and can coordinate through one or both the oxygen of the carboxyl group or through the phenoxy-oxygen and one of the oxygens of the carboxyl group. Prout *et al.*^{1,2} have established the presence of latter type of bonding in Cu(II) phenoxyacetates and monodentate nature of the ligand in Ni(II) complexes³. In the present note are described the preparation and characterization of a large number of metal(II) phenoxyacetates.

All the chemicals used were of reagent grade (BDH) and the ligands were prepared as reported in the literature^{4,5}.

Preparation of the complexes — All the complexes, except Mn(II), Co(II) and Hg(II) complexes, were obtained by the reaction of the corresponding metal (II) salts with a slight excess of either the free acid or the sodium salt of the acid in aqueous solution. In some cases 1 : 6 aq. ammonia was added to cause the precipitation. Mn (II) and Hg (II) derivatives were prepared by mixing an ethanolic or methanolic solution of the acid and that of the corresponding metal (II) acetates. For Co (II) complexes, 1:1 aq. alcohol was used as a solvent. The products were purified by

repeated washing with the solvent followed by sodium-dried ether and then dried in *vacuo*.

Most of the metal ions were estimated by EDTA titration. Cadmium and lead were determined as their sulphates and uranium as U_3O_8 . Magnetic susceptibility was measured at room temperature on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) in KBr were recorded on a Perkin-Elmer spectrophotometer and the electronic absorption spectra in nujol on a Carl-Zeiss UV-VIS-IR spectrophotometer. TG was performed on a stanton Redcraft thermobalance.

Elemental analyses and IR and magnetic moment data are presented in Table 1. The complexes of Mn(II), Fe(II), Co(II), Ni(II), Zn(II) and Hg(II) are soluble in water while those of Cu(II), Cd(II), Pb(II) and UO_2^{2+} are not. The insolubility of the complexes in common organic solvents indicate their probable polymeric nature. These complexes are non-conducting in DMF. The presence of water in the complexes was established by TG which indicated the loss of water around 120° . However, Cu(II), Ni(II) and Co(II) complexes lose their water molecules around 105° .

The magnetic moment values of Mn(II), Fe(II), Co(II) and Ni(II) complexes (Table 1) are normal and in good agreement with the values reported for octahedral spin-free complexes of these metal ions⁶. However *p*-methyl- and *p*-nitrophenoxy Fe(II) compounds have subnormal magnetic moments (~ 3.5 B.M.) indicating antiferromagnetic interaction⁷. All the Cu(II) complexes have magnetic moments in the range 2.0–2.2 B.M. which correspond to the presence of one unpaired electron and square-planar structure, uncomplicated by dimerisation. Evidently the square-planar structure is attained through chelation involving phenoxy-oxygen. X-ray crystal structure determinations^{1,2} on anhydrous and diaquobis(phenoxyacetato)copper (II) bear evidence to this.

The electronic spectra (ν_{max} in cm^{-1}) of all metal complexes except copper are characteristic of octahedral stereochemistry. Cobalt (II) complexes exhibit well-defined bands around 8300 and 21300 cm^{-1} which may be attributed to ν_1 and ν_3 transitions respectively. The less intense shoulder around 17500 may arise from ν_2 transition. All the Ni(II) complexes show ν_1 , ν_2 and ν_3 bands at 10210, 17540 and 27770 respectively. The band with double structure⁷ observed around 10650 and 8330 cm^{-1} for Fe(II) complexes is due to ${}^5E_g \leftarrow {}^5T_{2g}$ transition. The electronic spectra of all Cu(II) complexes display a broad band around 15300 which may be due to a combination of ${}^2A_{1g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$ transitions in D_{4h} symmetry⁸. Mn(II) complexes show continuous absorption in the visible region.

The IR spectra of (ν_{max} in cm^{-1}) the complexes exhibit characteristic bands in the region 1645–1540 ($\nu_{\text{as}}\text{COO}$) and 1445–1400 ($\nu_s\text{COO}$) (Table 1). The separation ($\Delta\nu$ 200–236 cm^{-1}) between these two bands for Cu(II) phenoxyacetates indicates unidentate acetate coordination involving phenoxy-oxygen in chelation^{1,2} (see structure I). $\Delta\nu$ 115–130 cm^{-1} for uranyl complexes corresponds to symmetrically chelated acetate as in structure (II) while $\Delta\nu$ 155–207 cm^{-1} for all the other complexes is diagnostic of bridged