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NOTE

Control of Mercury in Biological System

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Mercury is transported in the ecosystem by precipitation from the atmosphere to soil and water, uptake by plants and animals providing a constituent of bio-geochemical cycle. We have worked to reduce the mercury ions from the cycle with help of oxygen/nitrogen-containing compounds suitable to the ecosystem and thus helpful in reducing the toxicity of the biological system. In this direction we have synthesized $(DMF)_2Hg(Ox)_2$, $(DMA)_2Hg(Ox)_2$ and $(DMF)_2Hg(OAc)_2$, $(DMA)_2Hg(OAc)_2$ and supported by electrical conductance measurement, where DMF = dimethyl formamide, DMA = dimethyl acetamide, Ox = oxalate ion, OAc = acetate ion.

Key Words: Mercury, Biological system.

Mercury released to the environment as metal by losses from electrolytic cells used for NaOH and Cl_2 production or as compounds such as alkyl mercury seed dressings or fungicides constitutes a serious hazard[1].

Pictures of a snow-topped mountain and a lake in front in brilliant sunshine evoke the impression not only of a beautiful but also a clean environment. However such an environment is not as clean as many people like to think it is. In fact it never was due to the natural turnover of the elements[2–4]; for example in pre-industrial times, around 1890, approximately eight megamoles, *i.e.*, about 1600 tons of atmospheric mercury were turning around per year in the global mercury cycle involving sea and as well. In modern times, around 1990, the amount of mercury involved in the global cycle had approximately tripled due to human activities. Hence the amount in the atmosphere increased to about 25 megamoles, *i.e.*, *ca.* 5000 tons[5, 6]. Since this has been recognized steps are being undertaken to reduce the mercury burden worldwide, particularly in biological systems.

Being inspired by the above fact we undertook the work involving interaction of dimethyl formamide and dimethyl acetamide with mercuric oxalate and mercuric acetate compounds in methanolic medium.

The salts $Hg(Ox)_2$ and $Hg(OAc)_2$ have been prepared by dissolving HgO in the hot corresponding acid solution and crystallized. DMF (124°C) and DMA (123°C) were obtained from BDH. The salts were dissolved in excess of methanol.

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To the hot concentrated methanolic solution of salts, add DMF and DMA dissolved in toluene, step by step and after each addition the conductance was noted at 40°C in each case of $(DMF)_2Hg(Ox)_2$, $(DMF)_2HgO(Ac)_2$ and $(DMA)_2$ $Hg(Ox)_2$, $(DMA)_2Hg(OAc)_2$ complexes while these were in solution. The complexes were extracted in solid state using petroleum ether solvent.

The conductivities were determined by using dip type conductivity cell on a DC 610 conductivity meter. IR spectra were recorded on Perkin-Elmer in Nujol mull. Percentage of Hg was calculated by decomposition of the complex and separating Hg(II) salts using suitable gravimetric procedure.

The analytical data correspond to 1 : 2 (metal : base) stoichiometry. The adducts are thermally stable but decompose in the presence of moisture. The adducts formed by the interaction of $Hg(Ox)_2$ and $Hg(OAc)_2$ in methanolic medium with dimethyl formamide and dimethyl acetamide having formulae $(DMF)_2Hg(Ox)_2$, $(DMF)_2Hg(OAc)_2$ and $(DMA)_2Hg(Ox)_2$, $(DMA)_2HgO(Ac)_2$ are obtained. The compounds are reddish yellow in colour. The compounds are soluble in toluene.

The electrical conductance of salt $Hg(Ox)_2$ and $Hg(OAc)_2$ continuously being added in methanol show continuous increase. The electrical conduction may occur through the movement of either electrons or ions and the following basic equation may be employed,

$$\sigma = qn\mu$$

where the conductivity σ depends on three parameters: the charge q, concentration n, and the drift mobility μ of the charge carriers. In our case the drift mobility for methanol, the concentration of Hg(II) salts in methanolic medium increases and hence σ goes on increasing. But as we add DMF and DMA dissolved in toluene at regular intervals in equal instalments to the concentrated methanolic solution of $Hg(Ox)_2$ and $Hg(OAc)_2$, a continuous decrease in conductivity for the cationic exchange is obtained as the result of the stability of the new complex formation.

A rather convincing experimental verification of ionic association is found in a series of conductance studies made by Kraus and Fuoss[7]. They interpret their conductance curves in terms of ionic association. Basically, they assume that the decrease in conductance curves arises from the formation of ion pairs. This supports our observation; the percentage of Hg in case of $Hg(Ox)_2$ complexes with DMF and DMA is higher than that of $Hg(OAc)_2$ complexes. It shows the ion pair association to greater extent in the case of $Hg(Ox)_2$ comlexes compared to $Hg(OAc)_2$ complexes with the DMF and DMA. Thus fall in conductance in the case of $Hg(Ox)_2$ complexes is more comparable to $Hg(OAc)_2$ complexes. Further with DMF the fall in conductance of the complexes has been found more comparable to the complexes formed by DMA.

The ν(C═O) modes in various amide bases[8] (DMF, DMA) (1649 ± 17 cm^{-1}) undergo negative shift in the spectra of molecular adducts (1640 ± 15 cm^{-1}), suggesting coordination through the oxygen atoms of amide group with Hg.

The following table shows the compounds, colour, decomposition temperatures, percentage of Hg and elctrical conductance and IR bands.

TABLE-1
PHYSICAL, ANALYTICAL, CONDUCTANCE AND SPECTRAL DATA OF MERCURY(II) COMPOUNDS

Compound	Colour	Decomp. temp. (°C)	Hg (%)	Electrical conductance σ $(ohm^{-1})/cm^3$ at 40°C	IR Bands ν(C=O) (cm^{-1})
$Hg(Ox)_2$	Light yellow	—	70.0	(9.5×10^{-8})	1670
$Hg(OAc)_2$	Light yellow	—	62.9	(3.2×10^{-7})	1680
$(DMF)_2Hg(Ox)_2$	Reddish yellow	215	46.0	(6.1×10^{-9})	1635
$(DMA)_2Hg(Ox)_2$	Reddish yellow	205	43.3	(7.1×10^{-8})	1640
$(DMF)_2Hg(OAc)_2$	Reddish yellow	185	43.1	(2.4×10^{-9})	1650
$(DMA)_2Hg(OAc)_2$	Reddish yellow	170	40.8	(2.5×10^{-8})	1655

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