

URANIUM (IV) SUCCINATES AND TARTRATE

PHOTOCHEMICAL preparation of Uranium(IV) compounds¹ has shown that UO^{+2} ion is capable of forming a parallel series of compounds with that of normal Uranium(IV) ion U^{+4} though the number of compounds containing the Oxouranium (IV) entity, UO^{+2} , is limited. In continuation of our investigation on the preparation of Uranium(IV) compounds, we have isolated two compounds a succinate and a tartrate having the formula $\text{U}_2\text{O}(\text{C}_4\text{H}_4\text{O}_4)_3$ and $\text{U}_2\text{O}(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 5\text{H}_2\text{O}$ respectively which show that both the ionic species UO^{+2} and U^{+4} are present in the same compound. Besides an oxysuccinate, $\text{UO}(\text{C}_4\text{H}_4\text{O}_4) \cdot 3\text{H}_2\text{O}$ has also been prepared by photolytic method.

For the preparation of the simple oxysuccinate a photochemically reduced solution of uranyl formate was treated with succinic acid so that the ratio of Uranium(IV) to succinate ion was 1 : 3. The resulting solution was further exposed to sunlight for 10–12 hours when precipitation occurred and the light green succinate $\text{UO}(\text{C}_4\text{H}_4\text{O}_4) \cdot 3\text{H}_2\text{O}$ was obtained.

The Uranium (IV) succinate, $\text{U}_2\text{O}(\text{C}_4\text{H}_4\text{O}_4)_3$, containing both the ionic species, UO^{+2} and U^{+4} was obtained by the action of succinic acid solution in small quantities on hydrated uranium (IV) oxycarbonate⁷ till all the carbon dioxide gas was removed and the reaction was complete. The compound was readily obtained as a green precipitate.

The procedure adopted for the tartrate compound $\text{U}_2\text{O}(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 5\text{H}_2\text{O}$ was the same as the simple oxysuccinate. The analytical results are given in Table I.

TABLE I

Formula of the compound		% found	% calculated
$\text{UO}(\text{C}_4\text{H}_4\text{O}_4) \cdot 3\text{H}_2\text{O}$	Uranium	56.77	56.13
	Succinate	27.16	27.35
	Carbon	11.20	11.32
	Hydrogen	2.36	2.35
$\text{U}_2\text{O}(\text{C}_4\text{H}_4\text{O}_4)_3$	Uranium	50.43	50.68
	Succinate	41.39	42.07
$\text{U}_2\text{O}(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 5\text{H}_2\text{O}$	Uranium	45.80	46.40
	Tartrate	43.00	43.28
	Carbon	13.89	14.04
	Hydrogen	2.39	2.14

We have been unable to isolate any definite tartrate compound from Uranium(IV) oxy carbonate,

Chemistry Department, K. C. SATAPATHY.
M.P.C. College, Baripada,
and

Applied Chemistry Dept., B. SAHOO.
Indian Institute of Technology,
Kharagpur, February 2, 1967.

1. Sahoo, B. and Patnaik, D., *Curr. Sci.*, 1958, **27**, 243.
2. Patnaik, D. and Sahoo, B., *Ibid.*, 1958, **27**, 292.
3. Tripathy, K. K., Sahoo, B. and Patnaik, D., *J. Ind. Chem. Soc.*, 1959, **36**, 739.
4. Sahoo, B. and Patnaik, D., *Curr. Sci.*, 1960, **29**, 16.
5. Das, U. K., Pajari, S. K., Sahoo, B. and Patnaik, D., *Ibid.*, 1961, **30**, 380.
6. Sahoo, B., *Ind. J. Chem.*, 1964, **2**, 75.
7. — and Patnaik, D., *Nature*, 1960, **185**, 683.

ACTION OF 2-CHLORO-4-AMINO- BENZOIC ACID IN *OCHROMONAS* *MALHAMENSIS*

A VARIETY of sulphur-free compounds, structurally related to p-aminobenzoic acid, have been shown to possess antimicrobial activity.^{1–3} Out of a number of halogenated derivatives of p-ABA prepared by Wyss et al.,⁴ 2-chloro-4-aminobenzoic acid (2-Clp-ABA) was found to be as active as sulpha drugs in certain cases. But it was claimed that 2-Clp-ABA radically differed from sulphonamides in that this could be a specific inhibitor of methionine biosynthesis.⁴

With a view to elucidate the mode of action of this antimetabolite in *Ochromonas malhamensis*, its effect on growth and the folate status was determined. Details of growth conditions, folic acid extraction and estimation were as described by us in an earlier report.⁵

It was observed that, when included in the growth medium, 2-Clp-ABA did not interfere with folic acid metabolism in *O. malhamensis*, in spite of its being a structural analogue of p-AMA, a precursor of folic acid (Table I).

TABLE I

Effect of 2-Clp-ABA on the folate status of *O. malhamensis*

2-Clp-ABA $\mu\text{g.}$ per ml. of growth medium	Per cent. growth	Folic acid in $\mu\text{g.}$ per mg. dry weight of cells	
		Intra-cellular	Extra-cellular
0	100	2.24	8.6
50	71.8	2.16	7.9
100	30.6	2.02	7.8

Folic acid activity was measured with *S. faecalis* R as assay organism.

In view of this observation, alternate explanation had to be sought. An analysis of the culture filtrate of 2-Clp-ABA-inhibited cells showed that the added 2-Clp-ABA disappeared

from the growth medium, but could be recovered by acid hydrolysis with 0.5 M HCl at 100°C. for 1 hr. (Table II).

TABLE II
Metabolic fate of 2-Clp-ABA during the growth of *O. malhamensis*

2-Clp-ABA added to the medium $\mu\text{g. per ml.}$	Per cent. growth	2-Clp-ABA present in the medium after 7 days of growth $\mu\text{g. per ml.}$	
		Before hydrolysis	After hydrolysis
0	100
50	74.0	7.4	47
100	32.0	42.3	92
150	2.2	128.0	142

2-Clp-ABA was estimated by Bratton-Marshall reaction after deproteinising the culture filtrate with 10% trichloroacetic acid.

This is suggestive of some sort of binding of the amino group of 2-Clp-ABA. In this respect analogy could be drawn from the results of acetylation of *p*-ABA by animal liver observed by Harrow *et al.*⁶ It was also reported that the acute toxicity of sulphanilamide could be alleviated to some extent by a process of acetylation.⁷ This could be a possibility in the present case also. This supposition is further reinforced by reversal of growth inhibition due to *p*-ABA obtained with pantothenic acid during the present investigation.

On the basis of our observations it could be reasonably assumed that action of 2-Clp-ABA cannot be attributed to its interference in methionine synthesis alone. The acetylation of 2-Clp-ABA may be responsible for the growth inhibition, the acetylation mechanism in the organism being subjected to a greater strain, thus causing a depletion of acetyl CoA so vital for other metabolic functions of the organism. It seems 2-Clp-ABA has a preferential affinity to get acetylated rather than to compete with *p*-ABA in the biosynthesis of folic acid.

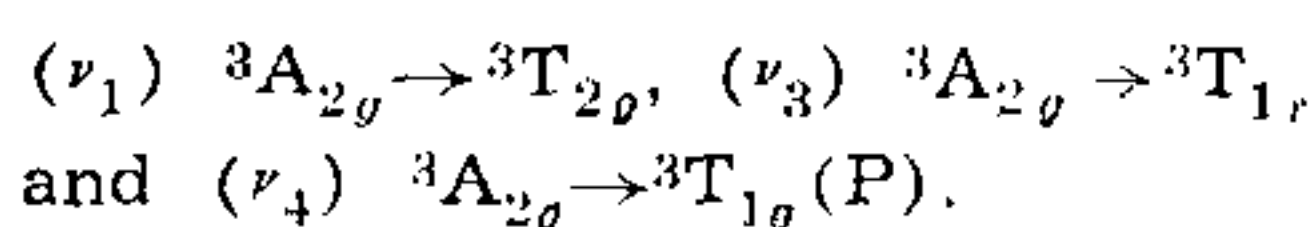
Dept. of Chemical Technology, V. H. POTTY,
University of Bombay, D. V. TAMHANE.
Matunga, Bombay-19, February 1, 1967.

CONFIGURATION EQUILIBRIA IN SOLUTION OF Ni (II) THIOMALIC ACID COMPLEXES

NICKEL (II) is known to form a deep violet coloured 1:3 (metal: ligand) complex with thiomalic acid, $\text{CH}_2\text{COOH}.\text{CHSHCOOH}$ (at pH 9.0 ± 0.2).¹ Mathur and Nigam² have reported the effective magnetic moment value 2.49 B.M. at 28.5°C. for this complex, whereas the value for an octahedral sp^3d^2 hybridised $\text{Ni}^{2+}(\text{d}^8)$ complex is expected³ to be 3.2–3.4 B.M. In trying to explain the observed anomaly in magnetic behaviour, Mathur and Nigam are inclined to believe that the covalency factor^{4,5} $+2$ (0.78 for the violet coloured complexes of Ni (II) and 0.92 for the green ionic complexes) might be responsible for quenching of magnetic moment.

In order to test the above points, the present authors have recorded the electronic spectra of this violet coloured complex in the range 1100–300 $\text{m}\mu$ (using Cary 14 recording spectrophotometer). The spectrum shows four bands at the positions $\nu_1 = 10337 \text{ cm.}^{-1}$, $\nu_2 = 16053 \text{ cm.}^{-1}$, $\nu_3 = 19802 \text{ cm.}^{-1}$ and $\nu_4 = 29850 \text{ cm.}^{-1}$.

Taking 10Dq value of an octahedral field from the first band in this case and using Ballhausen's equations⁶ the calculated bands are found to be 18594 cm.^{-1} and 28296 cm.^{-1} , which are fairly close to the observed positions of the bands ν_3 and ν_4 . The ratio of ν_3/ν_1 is equal to 1.9 which agrees with the theoretical value (1.8) for an octahedral complex. Assignments of the bands may be made as:



However, the covalency factor as calculated⁵ from spectral data comes out to be nearly 1.1 which clearly shows a completely ionic nature of the complex, and therefore the probability of covalency factor leading to a quenching in the magnetic moment, appears to be precluded. The planar form of Ni (II) complexes is known^{7,8} to have an absorption maximum at about 16000 cm.^{-1} . Recently,⁹⁻¹² a good amount of work has been done on the configuration equilibria in solution of Ni (II) complexes. Further, some workers⁹⁻¹¹ have observed reduction in magnetic moment, due to simultaneous occurrence of octahedral or tetrahedral species along with square planar, in the solution of Ni (II) complexes. A more probable explanation may therefore be found in the presence of another diamagnetic square planar species in equilibrium with the octahedral one

1. Hirsch, J., *Science*, 1942, **96**, 140.
2. Auhagen, E., *Z. Physiol. Chem.*, 1942, **276**, 48.
3. Kuhn, R., Möller, E., Wendt, G. and Beiner, H., *Ber. Chem. Ges.*, 1942, **75 B**, 711.
4. Wyss, O., Rubin, M. and Strandkov, F. B., *Proc. Soc. Expt. Biol. Med.*, 1943, **52**, 155.
5. Potty, V. H. and Tamhane, D. V., *J. Protozool.*, 1966, **13**, 501.
6. Harrow, B., Mazur, A. and Sherwin, C. P., *J. Biol. Chem.*, 1933, **102**, 35.
7. Wyss, O., Strandkov, F. B. and Schmelkes, F. C., *Science*, 1942, **96**, 236.