TABLE 3 — DETERMINATION OF Cd(II) IN THE PRESENCE OF Hg(II)

Hg(II) added (mg)	Cd(II) Taken (mg)	Cd(II) Found (mg)	Error (%)
10·030	2·754	2·751	−0·072
10·030	4·406	4·406	0·000
30·088	5·508	5·508	0·000
50·148	5·508	5·498	−0·183
50·148	8·262	8·262	0·000

The authors are grateful to Prof. W. Rahman for facilities, and to the CSIR, New Delhi, for financial assistance to one of them (D.K.S.).

References

1. BETLSTEIN, F. & JAWEIN, L., *Berichte der Busengesellschaft fur Kalische Chemie*, **12** (1879), 759.
2. DUVAL, C., *Inorganic thermogravimetric analysis* (Elsevier, Amsterdam), 1953.
3. TANANAEV, I. V. & KOZLOV, A. S., *Zhur. anal. Khim.*, **6** (1951), 149.
4. DESHMUKH, G. S. & VENUGOPALAN, M., *J. Indian chem. Soc.*, **33** (1956), 222.
5. BELCHER, R. A., NUTTEN, J. & STEPHEN, W. I., *J. chem. Soc.*, (1951), 3444.
6. THOMSON, T. L., *Ind. engng Chem. analyt. edn*, **13** (1941), 164.
7. BELLOMO, A., DEMARCO, D. & CASTLE, A., *Talanta*, **19** (1972), 1236.
8. SAUDBERG, B., *Svensk Chem. Tidskr.*, **58** (1946), 197.
9. FOULK, C. W. & BOWDEN, A. T., *J. Am. chem. Soc.*, **48** (1926), 2045.
10. REILLEY, C. N., SCHMID, R. W. & SADEK, FAWZYS, *J. chem. Educ.*, **36** (1959), 555.
11. KOLTHOFF, I. M., SANDELL, E. B., MEEHAN, E. J. & BRUCKENSTEIN, S., *Quantitative chemical analysis* (The Macmillan Co., London), IV edn, 1969, 800, 824.

Potentiometric Study of Complex Formation between Thiovanol & Th(IV), Zr(IV) & UO_2(VI)

K. M. KANTH*, K. B. PANDEYA† & H. L. NIGAM
Department of Chemistry, University of Allahabad
Allahabad

Received 13 *May* 1975; *revised* 5 *March* 1976; *accepted* 22 *May* 1976

Complex formation between thiovanol (1-thioglycerol) and Zr(IV), Th(IV) and UO_2(VI) has been studied potentiometrically. Formation of 1:2 (metal-ligand) complex has been observed in each case. The log K_1^H for thiovanol comes out to be 8·75. Stability constants of the metal complexes follow the order $Th^{4+} > Zr^{4+} > UO_2^{2+}$.

WE have recently reported[1-6] preparation and characterization of some transition metal complexes of thiovanol. The present note describes the results of *p*H-metric studies on complex formation of UO_2(VI), Zr(IV) and Th(IV) with thiovanol in solution.

TABLE 1 — METAL-LIGAND STABILITY CONSTANTS OF THE COMPLEXES

Metal ion	log K_1	log K_2	β_2	$\Delta F°$ (kcal/mole)
Zr^{4+}	6·60	2·25	8·85	−12·10
Th^{4+}	6·25	2·85	9·10	−12·49
UO_2^{2+}	5·95	2·20	8·15	−7·12

Thiovanol (Evans Chemetics, New York) was used as such. Its fresh solutions were prepared in doubly distilled water and estimated iodometrically. Stock solutions of metal ions were prepared from analytical grade reagents and standardized by usual methods (Th was precipitated as $[Th(C_2O_4)_2]$ and weighed as ThO_2; Zr, as $[ZrH_2(PO_4)_2]$ and weighed as ZrP_2O and UO_2 as $[UO_2(C_9H_6ON)_2 \cdot C_9H_7ON]$ and weighed as U_3O_8)[7]. A Leeds Northrup *p*H-meter fitted with a general purpose glass electrode was used for *p*H-measurements. All measurements were carried out at 25° in a nitrogen atmosphere. The following solutions were titrated against 0·1*M* NaOH solution: (i) 5 ml of 0·01*M* $HClO_4$ + 2·5 ml of 0·04*M* $NaClO_4$ + 42·5 ml water, (ii) 5 ml of 0·01*M* $HClO_4$ + 2·5 ml of 0·04*M* $NaClO_4$ + 2·5 ml of 0·009*M* thiovanol + 17·5 ml water, (iii) 5 ml of 0·01*M* $HClO_4$ + 2·5 ml of 0·04*M* $NaClO_4$ + 25 ml of 0·009*M* thiovanol + 2·5 ml of 0·01*M* metal ion (UO_2^{2+}, Th^{4+} or Zr^{4+}) + 15 ml water.

The plots of *p*H versus the volume of alkali added gave S-shaped curves. Values of $\bar{n}_H$, $\bar{n}$ and *pL* at different *p*H values were calculated using standard relationships[8-10]. All calculations were made below *p*H 5·0. Absence of hydrolytic side reactions was also confirmed. A $\bar{n}_H$ versus *p*H curve was obtained, which yielded the pK_{1H} value for thiovanol as 8·75. The values of log K_1 were directly read from the $\bar{n}$-*pL* formation curves and those of log K_2 were calculated using the method of Bjerrum[11] as modified by Irving and Rossotti[12] and Rossotti and Rossotti[10]. The results are presented in Table 1. The stabilities of thorium(IV) and zirconium(IV) complexes obey the Mellor and Maley order[11] ($Th^{4+} > Zr^{4+}$).

Thanks are due to Messrs Evans Chemetics Inc., New York, for supplying thiovanol as a gift sample.

References

1. NIGAM, H. L. & PANDEYA, K. B., *Indian J. Chem.*, **8** (1970), 454.
2. NIGAM, H. L., MATHUR, V. K. & PANDEYA, K. B., *Indian J. Chem.*, **9** (1971), 1292.
3. NIGAM, H. L. & PANDEYA, K. B., *Curr. Sci.*, **41** (1972), 449.
4. NIGAM, H. L. & PANDEYA, K. B., *Proceedings, chemistry symposium, Chandigarh*, Part 2, 1961, 147.
5. KANTH, K. M., PANDEYA, K. B. & NIGAM, H. L., *Indian J. Chem.*, **11** (1973), 103.
6. KANTH, K. M., PANDEYA, K. B. & NIGAM, H. L., *Indian J. Chem.*, **11** (1973), 1034.
7. VOGEL, A. I., *Quantitative inorganic analysis* (Longmans, Green, London), 1968, 539.
8. BJERRUM, J., *Metal-ammine formation in aqueous solutions* (Haase, Copenhagen), 1941, 152.
9. IRVING, H. M. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
10. ROSSOTTI, H. S. & ROSSOTTI, F. J. C., *Determination of stability constants* (McGraw-Hill, New York), 1961, 107.
11. MELLOR, J. W. & MALEY, G. F., *Nature, Lond.*, **159** (1947), 370; **161** (1948), 436.

*Present address: Department of Chemistry, R.D. & D.J. College, Monghyr, Bhagalpur University, Bihar.
†Present address: Department of Chemistry, University of Delhi, Delhi 110007.