

SOME MIXED LIGAND COMPLEXES OF ZIRCONIUM (IV), THORIUM (IV) AND URANIUM (VI)

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New thiocyanato complexes of Zr(IV), Th(IV) and U(VI) containing polydentate Schiff's base ligands derived from the condensation of salicylaldehyde with triethylene tetramine or 1, 3-diamino propane have been synthesized and characterized. The complexes have compositions, $[\text{Zr}(\text{SCN})_2\text{L}']$, $[\text{Th}(\text{SCN})_2\text{L}']$, $[\text{U}(\text{O})(\text{SCN})_2\text{L}']$, and $[\text{U}(\text{O})(\text{SCN})_2\text{L}']$, [schiff's base ligands, $\text{L}' = \text{N}_4\text{C}_8\text{H}_{16}(\text{C}_6\text{H}_4\text{OH})_2$; $\text{L}'' = \text{N}_2\text{C}_5\text{H}_8(\text{C}_6\text{H}_4\text{OH})_2$]. As per IR spectral data, the ambidentate thiocyanato ligand is N-coordinated suggesting that the metal centres behave as class a acceptors.

Thiocyanato complexes of transition metals containing Schiff's base ligands (Tarafer and Fatema 1988; Tarafer et al 1989; Tarafer et al 1990; Tarafer et al 1993) are important for the investigation of acceptor properties of such metals (Basolo et al 1964; Melpolder and Burmeister 1971; Lauer et al 1972) mainly because of their importance in preparative metallurgy (Tarafer et al 1981) but reports on thiocyanato complex of heavier metal ions are lacking (Isapkina and Ellert 1968; Cotton and Wilkinson 1988).

Reagent grade chemicals were used as supplied by BDH or Merck.

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Schiff's bases. Salicylaldehyde (0.04 mol) dissolved in absolute alcohol (30 cm³) was mixed with a solution of triethylene tetramine or 1, 3-diamino propane (0.02 mol) in the same solvent (30 cm³). To get L', this mixture was heated for 30 min at 40°C and the solution was kept at room temperature for 72 h; but for L'', the mixture was refluxed for 2.5 h and cooled in refrigerator for 48 h. The yellow precipitate formed (in both the cases) was collected by filtration, washed with ethanol and dried in vacuo oven P₄O₁₀ [M.P. 102.6°C (L'), 69.5°C (L'')].

Complexes 1-4. These were synthesized according to a common procedure. An ethanolic (methanolic for 1) solution (30-40 cm³) of KSCN (0.02 mol) was mixed with the appropriate hydrated metal nitrate (0.005 mol) dissolved in the same solvent (20-25 cm³). The precipitated KNO₃ was discarded and filtrate added to an ethanolic solution (20 cm³) of the Schiff's base L' to L'' (0.005 mol). The precipitate was filtered, washed with hot ethanol and finally dried in vacuo oven P₄O₁₀. C, H and N microanalyses were carried out by the microanalytical services at the University of Erlangen-Nurnberg, Germany. Zr, Th and U were determined by weighing as their oxides (Bagnall et al 1968).

IR spectra (as KBr discs, pressed, at atmospheric pressure) were recorded on a Pye-Unicam SP3-300 IR Spectrophotometer. Conductivities of 10⁻³M solutions of the complexes in DMSO were measured at 25°C using a WPA CM35 Conductivity Meter and a dip-type cell with platinized electrodes.

The analytical and conductivity data of the complexes are given in Table 1 and the IR spectral data in Table 2. Complexes 3 and 4 are soluble in DMSO and behave as 1:2 electrolytes while 1 and 2 are insoluble in DMSO. Measured melting/decomposition points of the complexes are found to be above 200°C. The metal ions in complexes 2 and 4 are six and seven

Table 1
Analytical data and other physical properties of the complexes**

No.	Compound	Colour	Metal (%)		Carbon (%)		Hydrogen (%)		Nitrogen (%)		Molar conductance Ω ⁻¹ cm ² mol ⁻¹
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
1	$[\text{Zr}(\text{SCN})_2\text{L}']$	Brick red	37.07	38.60	42.92	42.75	4.29	4.20	10.02	10.00	-
2	$[\text{Th}(\text{SCN})_2\text{L}']$	Reddish yellow	32.77	32.40	36.42	36.33	2.55	2.50	8.94	8.63	-
3.	$[\text{U}(\text{O})(\text{SCN})_2\text{L}']$	Yellow	36.48	36.90	36.59	36.31	3.32	3.27	11.63	11.56	76
4.	$[\text{U}(\text{O})(\text{SCN})_2\text{L}']$	Yellow	33.33	33.90	35.96	34.95	2.52	2.41	8.83	8.53	82

**The organic moieties for the compounds indicated are:

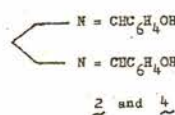
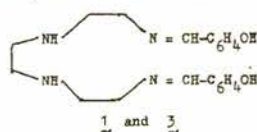


Table 2
IR spectral data of the complexes band maxima* (cm^{-1})

Complex No.	$\nu(\text{NH})$	$\nu(\text{CN})$	$\nu(\text{C=N})$	$\nu \text{U=O}$	$\nu(\text{C=S})$	$\nu(\text{M-O})$	$\nu(\text{M-N}')$	$\nu(\text{M-N})$
1.	3250	2055vs	1530s	-	760m	440vw	330vw	310w
2	-	2080s	1530w	-	720s	450m	330w	310w
3	3220	2060vs	1530vs	905 vs	765vs	405vw	355w	300w
4	-	2080m	1510vs	910vs	-	410w	330w	-

*Relative band intensities are denoted by s, vs, m, w and vw meaning strong, very strong, medium, weak and very weak respectively. ($\text{N}' = \text{Nitrogen of NCS}$).

coordinated while in **1** and **3** are eight and nine coordinated respectively. The Schiff's bases L' and L'' are potentially hexadentate dinegative and tetradentate-dinegative ligands (Table 1).

In the IR spectra of the complexes, **1-4** the lower $\nu(\text{NH})$ values compared to free $\nu(\text{NH})$ value together with the observed $\nu(\text{M-O})$ modes at $450\text{-}410\text{ cm}^{-1}$ (Westland and Tarafder 1981) and $\nu(\text{M-N})$ and $310\text{-}300\text{ cm}^{-1}$ (Tarafder *et al* 1981) indicate that the Schiff's base ligands are coordinated through their oxygen and nitrogen atoms. The uranium complexes **3** and **4** display IR bands at 905 and 910 cm^{-1} arising from $\nu(\text{U=O})$ modes (Westland and Tarafder 1981). Further, the $\nu(\text{CN})$ and $\nu(\text{M-N}')$ bands ($\text{N}' = \text{nitrogen of NCS moiety}$; $\text{M} = \text{metal atom}$) at $2080\text{-}2050\text{ cm}^{-1}$ and $355\text{-}330\text{ cm}^{-1}$ respectively as well as the $\nu(\text{CS})$ bands at $770\text{-}720\text{ cm}^{-1}$ are indicative of the N-bonded SCN moieties (Pauling 1964; Vleek 1970; Wittenburg and Wittenburg 1970; Lauer *et al* 1972). This is in agreement with the "hard acid" character of the Zr(IV), Th(IV) and U(VI) which behave as class a acceptors despite the donor properties of the auxiliary ligands used. The primary valencies of the metals, therefore, determine their acidity.

Key words: Mixed ligand complexes, Heavy metals, Schiff's bases

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