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Complexes of 2-Thiouracil with Some Divalent Metal Ions

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Simple complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 2-thiouracil (TU) have been prepared and characterized by various physico-chemical methods. IR results show that 2-thiouracil is bidentate in all cases, coordinating through sulphur and one nitrogen atom. The X-ray powder pattern of the complexes suggests orthorhombic symmetry for Mn(II)-2TU, Co(II)-2TU, Mi(II)-2TU, Zn(II)-2TU and tetragonal symmetry for Cu(II)-2TU complexes.

INTRODUCTION

The pyrimidine 2-thiouracil (2–TU), a sulphur containing analogue of uracil, which occurs naturally in transfer ribonucleic acid and the interaction of metal ions with *t*RNA is of importance in protein synthesis and consequently cell growth[1]. 2-Thiouracil is also of physiological importance as a well known antithyroid agent[2]. Its complexes with some metal ions have been reported in the literature[3–5]. The present investigation reports the interaction between metal ions viz. Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and 2-thiouracil and the detailed characterzation of isolated complexes.

EXPERIMENTAL

Preparation of Complexes

1 mmol of the metal nitrates hydrated were dissolved in a mixture of 15 ml triethylorthoformate and 35 ml ethanol by refluxing for 4 hrs. Then, 1 mmol of 2-thiouracil was added and the resultant mixture was refluxed until a substantial amount of the precipitated complex had accumulated. Subsquently, the volume of supernatant was reduced to about one-half of its original volume by heating and the new complexes were precipitated by adding ether. The solid complexes were filtered, washed several times with ethanol, finally with ether and dried at 50–60°C.

The metal ions were determined by EDTA titrations after dissolving the complexes in dilute nitric acid. Carbon, hydrogen and nitrogen were analysed by microanalytical lab using a Perkin-Elmer model 240C elemental analyser. Infrared spectra (4000–200 cm^{-1}) were obtained in solid state with Perkin-Elmer 783 spectrophotometer and the electronic spectra were registered on a UV/VIS-

168A spectrophotometer at room temperature. The room temperature magnetic susceptibilities were measured with a Cahn Faraday magnetic susceptibility balance. X-ray powder diffraction studies were performed on a Philips PW 1710 diffractometer using Cu-K_α radiation.

RESULTS AND DISCUSSION

The composition of the complexes, analytical data and other physical properties are listed in Table 1. All the complexes are coloured except Zn(II) and Cd(II) and display 1 : 2 stoichiometry. The solubility of these complexes in most organic solvents is not very good even on heating. Mn(II)-2TU and Zn(II)-2TU have melting point in the range 270 to 290°C, whereas other complexes do not melt up to 300°C.

TABLE 1
ANALYTICAL DATA AND OTHER PROPERTIES OF COMPLEXES

Complexes	Calculated (Found %)				M.pt. (°C)	μ_{eff} B.M.
	M	C	H	N		
$Mn(2\text{–}TU)_2 \cdot H_2O$	15.82	27.64	3.45	16.12	270	5.70
Light yellow	(15.86)	(27.58)	(3.41)	(16.08)		
$Co(2\text{–}TU)_2 \cdot H_2O$	16.77	27.33	3.41	15.94	> 300	5.27
Light pink	(16.72)	(27.37)	(3.46)	(15.90)		
$Ni(2\text{–}TU)_2 \cdot H_2O$	16.72	27.35	3.41	15.95	> 300	3.43
Light green	(16.76)	(27.39)	(3.39)	(15.91)		
$Cu(2\text{–}TU)_2 \cdot H_2O$	17.84	26.98	3.37	15.73	> 300	1.78
Bluish green	(17.80)	(26.93)	(3.34)	(15.70)		
$Zn(2\text{–}TU)_2 \cdot 2H_2O$	28.48	20.91	3.48	12.19	288	–
White	(28.42)	(20.95)	(3.44)	(12.13)		
$Cd(2\text{–}TU)_2 \cdot 2H_2O$	27.77	23.72	2.96	13.83	> 300	–
White	(27.74)	(23.75)	(2.92)	(13.86)		

Some relevant IR frequencies of 2-thiouracil and its metal complexes are given in Table 2. The bands at 3190 cm^{-1} and 3130 cm^{-1} have been tentatively assigned to νN–H vibration of 2-TU, which are absent in the infrared spectra of some complexes and appear to be shifted toward lower wave numbers in other complexes. For all these compounds, δN_3–H band decreases in intensity and position or completely disappears from the spectra whereas δN_1–H remains constant in intensity and position, pointing to N_3 coordination. The spectrum of free ligand has infrared absorptions at 1712 cm^{-1} and 1682 cm^{-1}, which have been assigned as νC=O, νC=C bands. Only minor changes are observed for the position of these bands after complexation. The thioamide band I at 1560 cm^{-1} in 2-TU is suggested to be more sensitive to coordination than the two low frequencies νC=S bands (at 1172 and 1155 cm^{-1})[4,7]. In the infrared spectra of complexes the thioamide band I (1560 cm^{-1}) has been shifted as shown in Table 2,

TABLE 2
RELATIVE INFRARED ABSORPTIONS DATA (cm^{-1}) FOR 2-THIOURACIL AND ITS COMPLEXES

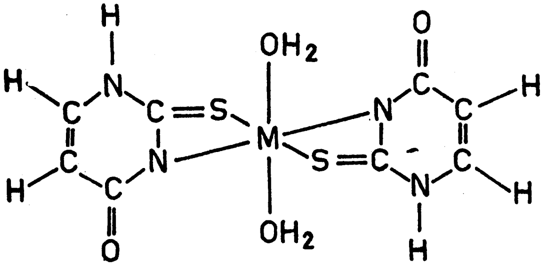
Band assignment	2-TU	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
νO–H	—	3350 w	3430 w	3430 w	3430 w	3335 w	3420 m
νN–H	3190 m	3150 w	—	3120 w	3150 w	3160 w	3160 m
	3130 w	—	—	3110 w	3110 w	—	3115 m
νC=O, νC=C	1712 m	1710 m	1710 w	1710 s	1708 w	1705 w	1710 w
	1682 m	1678 m	1668 w	1678 w	1680 w	1675 w	1685 w
νC=S	1560 s	1570 s	1580 w	1575 s	1525 m	1575 m, b	1530 s
	1172 s	1160 s	1180 w	1179 m	1175 w	1172 w	1180 m
	1155 m, b	—	1165 w	1160 s	—	1160 w	1170 m
δN_1–H	1505 s	1505 w	1505 w	1502 m	1508 s	1505 m, b	1505 m
δN_3–H	1422 w	1394 m	1410 m, b	1410 s	1405 m	1395 s	—
νM–O_{aquo}	—	385 m	420 m	418 w	425 w	355 m	355 s
νM–N	—	275 m	275 m, b	275 w	295 m	285 w	280 m

which may be indicative of bonding through the sulphur atom to the metal centres. All these complexes show infrared bands in the 3500–3250 cm^{-1} region, attributed to νO–H of water[8]. Bands assigned to νM–O_{aquo} bands in lower region suggest the binding of water molecules in the complexes[9]. The tentatively assigned νM–N bands favour coordination number six for the metal ions in all these compounds[8,10].

The magnetic moment of Mn(II) complexes is 5.70 B.M. The electronic spectrum shows bands at 300 nm, 390 nm and 535 nm which favours octahedral structure[11]. The electronic spectrum of Co(II)-2TU exhibits bands at 440 nm, 1225 nm. The magnetic moment value 5.27 B.M. suggests octahedral geometry around Co(II)[12]. The electronic spectral bands at 420 nm, 660 nm and 1275 nm favour octahedral geometry around Ni(II), which has the magnetic moment value 3.43 B.M.[13] The magnetic moment value of Cu(II) compound is 1.78 B.M. showing the presence of one unpaired electron. The occurrence of d–d transition band at 516 nm favours distorted octahedral geometry for Cu(II)–2TU complex[12].

X-ray diffraction data have been successfully indexed. The indexing of the pattern was done by Ito's method[14]. A careful study of the powder pattern revealed the structure as orthorhombic for Mn(II)–2TU, Co(II)–2TU, Ni(II)–2TU, Zn(II)–2TU and as tetragonal for Cu(II)–2TU complex. The indexing of the pattern yields lattice constants $a = 8.14$, $b = 6.02$ and $c = 5.82$ Å for Mn(II)–2TU, $a = 4.92$, $b = 4.59$ and $c = 4.30$ Å for Co(II)–2TU, $a = 7.42$, $b = 4.97$ and $c = 4.82$ Å for Ni(II)–2TU, $a = b = 12.48$ and $c = 14.00$ Å for Cu(II)–2TU, $a = 15.30$, $b = 5.79$ and $c = 5.06$ Å for Zn(II)–2TU.

On the basis of above studies, the structure of the complexes may be proposed as follows.



M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)

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