Inorganica Chimica Acta, 37 (1979) L505–L506

Complexes of 2-Thiouracil with Some Divalent Metal Ions

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Received June 26, 1979

As part of our work on the coordination of pyrimidine [1] and purine [2] derivatives to metal ions we report here some complexes formed by 2-thiouracil (tura). This ligand is of interest because of its therapeutic activity [3] and because it is one of the thio-bases that occur in sRNA and tRNA.

Agarwala and co-workers [4, 5] reported some inner complexes of thiouracils in which partial or complete deprotonation of the ligands had occurred and more recently Nelson and Villa have described Cu(dithiouracil)(OH)·H_2O, Cu(2-thiocytosine)Cl_2 and Cu(2-thiocytosine)$_2Cl_2$·$4H_2O$ [6].

The compounds we have isolated are listed in Table I.

With the metal halides studies, all except the cobalt(II) halides gave 2:1 complexes with tura. Attempts to make the corresponding cobalt complexes always resulted in Co(tura)$_4X_2$ (X = Cl, or Br) which, from the low intensities of their electronic spectral bands (Table II), have *trans*-octahedral structures. Proton migration from N1 or N3 and consequent formation of a CoN_4X_2 chromophore are ruled out by the low energy (~7000 cm^{-1}) and lack of any significant splitting of the first spin-allowed band, in comparison with complexes such as Co(4-methylpyridine)$_4Cl_2$ [7].

Although uracil itself is known to coordinate to metal ions via exocyclic oxygen [8] the donor ability of thione sulphur atoms is generally greater than such ketonic groups and it is likely that in Co(tura)$_4X_2$ the thiouracil binds via sulphur. The low frequency i.r. spectrum of Co(tura)$_4Cl_2$ had a medium strong band at 229 cm^{-1} assignable to ν(Co–Cl) and another band at 237 cm^{-1}, which was also present for the bromide analogue at 236 cm^{-1}, but was absent from the spectrum of tura. These last two bands may be reasonably assigned to ν(Co–S) (though we recognize the approximate nature of such a designation for a mode which will probably have only partial ν(Co–S) character). However, it may be noted that, although ν(M–O) bands are generally at higher energies, bands in the range 225–245 cm^{-1} have been assigned to metal–oxygen stretches in some uridine complexes [9].

The electronic spectra of the nickel complexes Ni(tura)$_2X_2$ (X = Cl or Br) are typical of six-coordination with a weak ligand field. The halide dependence of the band energies suggests that the halides are coordinated but their far i.r. spectra (Table II) do not permit a reliable differentiation between bridging halide or bridging tura arrangements. The manganese complexes Mn(tura)$_2X_2$ (X = Cl or Br) are also polymeric as their X-band e.p.r. spectra show simply a broad band at $g_{eff} \approx 2$. The absence of ν(Mn–X) bands above 200 cm^{-1} suggests that polymerisation in these compounds is by halide bridges.

The far i.r. spectra of Zn(tura)$_2Cl_2$ includes a set of three strong bands at 287, 319 and 337 cm^{-1} two of which may be assigned as ν(Zn–Cl) of a tetrahedral complex. The 287 cm^{-1} band is clearly the lower frequency ν(Zn–Cl) mode but, as the 302 cm^{-1} ligand band ranges from 308 to 339 cm^{-1} in the other complexes studied, we cannot be certain which of the 319 and 337 cm^{-1} bands is ν_{as}(Zn–Cl). The 215 cm^{-1} band is tentatively assigned as ν(Zn–S) by comparison with the results for tetrahedral Zn(thiourea)$_2Cl_2$ [10] and allowing for increased ligand mass. The absence of any ν(Hg–X) bands above 200 cm^{-1} rules out a tetrahedral geometry for the mercury(II) analogue. The X-ray powder patterns of the complexes M(tura)$_2Cl_2$ (M = Zn, Cd, and Hg) are completely different.

TABLE I. Analytical Data for Some Complexes of 2-Thiouracil (tura).

Complex	Colour	Found (%)			Calculated (%)		
		C	H	N	C	H	N
Mn(tura)$_2Cl_2$	White	25.14	2.21	14.26	25.14	2.11	14.66
Mn(tura)$_2Br_2$	White	20.49	1.64	11.56	20.40	1.71	11.89
Co(tura)$_4Cl_2$	Pink	29.78	2.44	16.85	29.91	2.51	17.44
Co(tura)$_4Br_2$	Pink	26.64	2.20	15.20	26.28	2.21	15.32
Ni(tura)$_2Cl_2$	Yellow	25.08	2.27	14.30	24.90	2.09	14.52
Ni(tura)$_2Br_2$	Orange	20.63	1.74	11.33	20.24	1.70	11.80
Zn(tura)$_2Cl_2$	White	24.31	2.07	13.98	24.48	2.05	14.27
Cd(tura)$_2Cl_2$	White	22.14	1.85	12.48	21.86	1.83	12.74
Hg(tura)$_2Cl_2$	White	18.56	1.51	10.54	18.21	1.53	10.62

TABLE II. Spectral Data (cm^{-1}) for Some Complexes of 2-Thiouracil (tura).

Compound	IR Spectra[a]	Electronic (Reflectance) Spectra
tura	302s	–
$Mn(tura)_2Cl_2$	227 s 339s	–
$Mn(tura)_2Br_2$	224s 334s	–
$Co(tura)_4Cl_2$	229ms 237ms 308s	20,100sh 18,200 14,800 wsh 7100br
$Co(tura)_4Br_2$	236ms 309s	19,600sh 17,700 14,500sh 6850
$Ni(tura)_2Cl_2$	235s 251s 316s	23,750 20,800wsh 13,500 8250
$Ni(tura)_2Br_2$	228w 246m 316s 330s	23,700sh[b] 19,450wsh 12,300 7250
$Zn(tura)_2Cl_2$	215m 287s 319s 337s	–
$Cd(tura)_2Cl_2$	221s 317s	–
$Hg(tura)_2Cl_2$	315s	–

[a] 200–400 cm^{-1}. [b] On edge of strong u.v. band.

Experimental

The complexes were prepared by refluxing (24–48 hr) the appropriate metal salt with 75% of the required stoichiometric amount of 2-thiouracil in ethyl acetate containing a small quantity of 2,2-dimethoxypropane. The reaction mixture was protected from atmospheric moisture as most of the solids were somewhat hygroscopic. They were dried *in vacuo* at 100 °C. Microanalyses were by the Microanalytical Laboratory, Imperial College.

Physical measurements were carried out as described previously [2].

Acknowledgements

We thank the Science Research Council for a Research Studentship to G.A.L.

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