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Complexing Behaviour of 2-Thioorotic Acid: Complexes of Co(II), Fe(II), Rh(III), Pd(IV) & Pt(IV)

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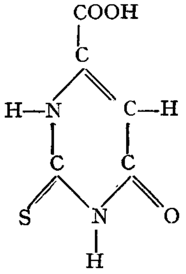
Complexes of 2-thioorotic acid have been prepared with Co(II), Fe(II), Rh(III), Pd(IV) and Pt(IV). Their probable structures have been postulated on the basis of magnetic moments, electronic and infrared spectra. Crystal field parameters have been calculated.

In our previous communications[1,2] we have shown our interest in the study of the complexing behaviour of 2-thioorotic acid (I):



(I)

This compound and its salts have a number of therapeutic[3-5] and industrial[6-8] applications.

In this paper the preparation and spectral and magnetic properties of the complexes of Co(II), Fe(II), Rh(III), Pd(IV) and Pt(IV) with (I) are reported.

Materials and Methods

All the chemicals used were of AR or CP grade.

2-Thioorotic acid (I) (abbreviated as H_2tot) was prepared by the method described in the literature[9-11]. The ammonium and sodium salts of (I), abbreviated as AmHtot and NaHtot respectively, and their deuterated forms were prepared by a procedure described in our previous communication[1].

Preparation of the complexes: (I) *Bis*(2-*thioorotato*) (*diaquo*) *cobalt*(*II*) — A solution of 1·2 g (~5 mmoles) of $CoCl_2.6H_2O$ in 30 ml water was added to a solution of 1·9 g (~10 mmoles) of AmHtot in 100 ml water. The mixture was refluxed for 2 hr when a grey precipitate was formed. It was centrifuged and washed repeatedly with warm water.

The deuterated complex was prepared by an identical procedure except that D_2O and sodium salt of the ligand were used in the place of H_2O and AmHtot.

(II) (2-*Thioorotato*) (*ammine*) (*triaquo*) *cobalt*(*II*) — A solution of 0·6 g (~2 mmoles) of $Co(NO_3)_2.6H_2O$ in 20 ml water was added to a solution of 0·4 g (~2 mmoles) of the ligand (H_2tot) in excess of dil. ammonia (30 ml). After concentrating the mixed solution to nearly one-fourth of its volume, excess of acetone was added, when a dark brown precipitate was formed which was centrifuged, redissolved in the minimum quantity of water and reprecipitated by acetone. The complex was centrifuged and washed with a little water.

(III) (2-*Thioorotato*) (*pyridine*) (*triaquo*) *cobalt*(*II*) — A solution of 0·4 g (~1·5 mmoles) of $Co(NO_3)_2.6H_2O$ in 20 ml pyridine was added to a solution of 0·2 g (~1 mmole) of the ligand (H_2tot) in 20 ml pyridine containing approximately 0·2 ml water. On mixing the two solutions, an intense pink colour developed. The solution was slowly evaporated when pink coloured crystals were formed. These crystals were separated by centrifugation and washed with acetone.

(IV) (2-*Thioorotato*) (*dipyridine*) (*diaquo*) *cobalt*(*II*)— The method of preparation of this complex was similar to that described in (III), except that the metal salt and the ligand were mixed in 1:1 ratio, pyridine was used in large excess, and the contents were boiled for 15 min and then digested on a water-bath for 4 hr. A light brown complex was obtained.

(V) (2-*Thioorotato*) (*aniline*) (*aquo*) *cobalt*(*II*) — A solution of 0·5 g (~2 mmoles) of $CoCl_2.6H_2O$ in 20 ml water was added to a warm solution of 0·7 g (~4 mmoles) of the ligand (H_2tot) in a solvent mixture containing aniline (50 ml) and ethanol (10 ml). The resulting solution was evaporated nearly to dryness on a water-bath. The black residue obtained was washed with a large quantity of absolute ethanol followed by 50% ethanol.

(VI) (2-*Thioorotato*) (*methylaniline*) (*aquo*) *cobalt*(*II*)— The preparation of this complex was similar to that described in (V) except that methylaniline was used in the place of aniline. The complex was black in colour.

(VII) *Bis*(2-*thioorotato*) (*aminopyridine*) (*diaquo*) *cobalt*(*II*) — A solution of 1·4 g (~6 mmoles) of $CoCl_2.6H_2O$ in 50 ml water was mixed with another solution of 2·1 g (~12 mmoles) of the ligand (H_2tct) and 2·3 g (~24 mmoles) of aminopyridine in 180 ml of 80% ethanol. The resulting solution was digested

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for 2 hr on a water-bath and then left overnight when a brownish black precipitate was formed. It was centrifuged and washed with ethanol.

(VIII) *(2-Thioorotato) (triethylamine) (tetraaquo)-cobalt(II)* — A solution of 2·4 g (~10 mmoles) of $CoCl_2.6H_2O$ in 50 ml water was added to a warm solution of 1·7 g (~10 mmoles) of the ligand (H_2tot) in a solvent mixture containing 100 ml ethylamine and 24 ml of ethanol. An intense red-brown colour of the solution developed. It was evaporated nearly to dryness on a water-bath. A few ml of water were added to the residue and it was warmed to get a clear solution. To this solution, excess of acetone was added when a dark-brown complex precipitated out. It was centrifuged out and washed with acetone.

(IX) *(2-Thioorotato) (quinoline) (aquo) cobalt(II)* — A solution of 1·9 g (~8 mmoles) of $CoCl_2.6H_2O$ in 30 ml water was added to a warm solution of 1·4 g (~8 mmoles) of the ligand in a solvent mixture containing quinoline (50 ml) and ethanol (35 ml). The resulting solution was digested on a water-bath for 2 hr when a black precipitate appeared. It was allowed to stand overnight. Excess of ethanol was added to the mixture and the residue separated by centrifugation and washed with excess of ethanol.

All the complexes were dried at 110°.

Complexes of iron, rhodium, platinum and palladium — (X) Bis(2-thioorotato) (tetraaquo) iron(II); (XI) bis(2-thioorotato) (diaquo) rhodium(III); (XII) bis(2-thioorotato) (diaquo) platinum(II); and (XIII) tris(2-thiorotato) (dichloro) (tetraaquo)dipalladium(IV) were prepared by mixing in stoichiometric ratio solution of metal ion [$Fe(SO_4)(NH_4)_2SO_4.6H_2O$, Na_2PtCl_6 and K_2PdCl_6 in water and $RhCl_3.xH_2O$ in ethanol] and an aqueous solution of NH_4Htot. The reaction mixture was digested for 2 hr in each case. The complexes of Fe(II) and Pt(IV) were centrifuged out while the soluble complexes of Rh(III) and Pd(IV) were evaporated to dryness. All the complexes were dried at 110°.

Preparation of deuterated complexes—The deuterated forms of the complexes (XI), (XII) and (XIII) were prepared by refluxing 0·2 g of the respective complex in 20 ml D_2O for about 2 hr. D_2O was removed by evaporating the solution to dryness. The complexes were finally dried at 110°.

Analyses — Sulphur in the complexes was estimated by fusing a known amount of the compound in a mixture of KNO_3 and KOH (1 : 8, w/w) followed by extraction with distilled water, acidification with HNO_3 and estimation of sulphate ion as $BaSO_4$[12]. Analyses of Co, Fe, Pd, Pt and Rh in the respective complexes were carried out by decomposing the complexes by aqua regia followed by evaporation to dryness, extraction with water and estimation of metal ions by standard methods[12,14]. Carbon, hydrogen and nitrogen were analysed by the Microanalytical Section of the Indian Institute of Technology, Kanpur.

Molecular weights of water soluble complexes were determined by cryoscopic method.

Results and Discussion

The analytical data (Table 1) indicate that the metal ions, except Pd(IV), form two types of complexes: (a) $ML_2(H_2O_x)(X)_y$ and (b) $ML(H_2O)_a(X)_b$. Pd(IV) forms complex of the type $Pd_2L_3Cl_2.4H_2O$.

TABLE 1 — ANALYTICAL DATA AND MAGNETIC MOMENTS OF THE COMPLEXES

Complex	Calc. (Found), %					μ_{eff} (BM)
	C	H	N	S	M	
$Co(C_5H_3N_2O_3S)_2(H_2O)_2$	27·5	2·3	12·8	14·6	13·4	4·9
	(27·5	2·3	12·8	14·3	12·9)	
$Co(C_5H_2N_2O_3S)(NH_3)(H_2O)_3$*	20·0	3·3	13·9	10·6	19·6	3·75
	(20·6	3·2	13·8	10·4	20·3)	
$Co(C_5H_2N_2O_3S)(C_5H_5N)(H_2O)_3$*	33·1	3·5	11·6	8·8	16·3	—
	(32·7	3·3	11·7	8·2	16·6)	
$Co(C_5H_2N_2O_3S)(C_5H_5N)_2(H_2O)_2$*	42·3	3·8	13·2	7·5	13·9	4·4
	(42·9	4·0	13·6	7·3	14·4)	
$Co(C_5H_2N_2O_3S)(C_6H_7N)(H_2O)$	38·9	3·2	12·4	9·4	17·4	3·75
	(38·4	3·0	12·0	9·9	17·8)	
$Co(C_5H_3N_2O_3S)(C_7H_9N)_2(H_2O)_2$	49·4	4·8	12·1	6·9	12·8	4·4
	(49·1	4·6	12·4	7·0	13·3)	
$Co(C_5H_3N_2O_3S)_2(C_5H_6N_2)(H_2O)_2$	33·9	3·0	15·8	12·0	11·0	4·4
	(34·4	3·2	16·3	11·5	10·5)	
$Co(C_5H_2N_2O_3S)(C_6H_{15}N)(H_2O)_4$*	32·7	6·1	10·4	8·0	15·0	4·2
	(31·9	5·8	10·8	8·3	15·9)	
$Co(C_5H_2N_2O_3S)(C_9H_7N)(H_2O)$	44·0	3·4	11·1	8·4	15·8	4·5
	(43·6	3·14	11·2	8·6	15·0)	
$Fe(C_5H_3N_2O_3S)_2(H_2O)_2$	26·5	3·1	12·4	14·1	12·4	5·3
	(26·2	3·0	12·2	13·8	13·0)	
$Rh(C_5H_{2\frac{1}{2}}N_2O_3S)_2(H_2O)_2$	25·0	2·0	11·6	13·3	21·4	Diamagnetic
	(24·4	2·6	12·0	13·7	20·8)	
$Pd_2(C_5H_2N_2O_3S)_3Cl_2(H_2O)_4$†	20·8	1·6	9·7	11·1	24·6	do
	(20·9	2·1	9·2	10·8	26·4)	
$Pt(C_5H_2N_2O_3S)_2(H_2O)_2$	20·9	1·4	9·7	11·2	34·1	do
	(20·4	1·3	9·2	11·7	33·6)	

*Molecular weight determination showed monomeric nature of the complex.
†Cl was also estimated.

Magnetic Moment

The complexes of Rh(III), Pd(IV), and Pt(IV) are diamagnetic as expected for octahedral complexes of these metal ions[15]. The magnetic moment of Fe(II) complex (determined by the Gouy method) is 5·2 BM. This value is well within the acceptable range for octahedral Fe(II) complexes[16]. The magnetic moments of the present Co(II) complexes lie in the range 3·75-4·9 BM. While the values around 4·9 BM indicate octahedral coordination, values around 3·75 BM. may be due to tetrahedral field or tetragonal distortion of the octahedral geometery[15-19]. Tetrahedral Co(II) complexes should not show magnetic moments below 3·87 BM, therefore, tetragonally distorted octahedral structures are assigned to the present complexes. This is in conformity with the results of electronic spectra also.

*Electronic Spectra**

Cobalt complexes — In the electronic spectra of high-spin octahedral complexes of Co(II), one should expect three bands corresponding to the transitions ${}^4T_{1g}\rightarrow{}^4T_{2g}$; ${}^4T_{1g}\rightarrow{}^4A_{2g}$ and ${}^4T_{1g}\rightarrow{}^4T_{1g}(P)$. In tetrahedral complexes, three bands corresponding to the transitions ${}^4A_{2g}\rightarrow{}^4T_{2g}$, ${}^4A_{2g}\rightarrow{}^4T_{1g}(F)$, and ${}^4A_{2g}\rightarrow{}^4T_{1g}(P)$ should appear. One can distinguish between the two geometries on the basis of (i) relatively larger value of the extinction coefficient, (ii) presence of a band in the near infrared region (5000-8000) and the absence of any *d-d* transition band around 25000 in the spectra of the tetrahedral complexes. In octahedral complexes, the ratio of the $\nu_2({}^4T_{1g}(F)\rightarrow{}^4A_{2g})$ and $\nu_1({}^4T_{1g}\rightarrow{}^4T_{2g})$ should lie in the range 2·1-2·2 (ref. 20).

The electronic spectral band positions and their respective assignments along with the values of crystal field parameters of Co(II) complexes are given in Table 2. Using these values of *Dq* and B, the positions of the second band (ν_2) were calculated in every case. These values correspond well with those found experimentally. The ratios of ν_2 and ν_1 calculated for each complex lie in the range 2·1-2·2. The extinction coefficients of the bands lie below 100. The values of 10 *Dq* are well within the range found for the other Co(II) complexes, and approximately similar to the values of 10 *Dq* found for octahedral Ni(II) complexes with the same ligand[20]. All these observations suggest octahedral geometry of the ligands around Co(II) ion in the complexes. In some cases the values of B calculated by assuming tetrahedral geometry were found to be more than the free ion value ($B_0=1120$). Besides, no band was observed around 4000 in any of the cobalt complexes.

The values of β for the complexes lie in the range 0·8-0·95 which are similar to those found for Ni(II) complexes with the same ligand[1]. This indicates the bonding in these complexes to be predominantly ionic which one should expect in the case of Co(II)

TABLE 2 — ELECTRONIC BANDS, THEIR ASSIGNMENTS AND CRYSTAL FIELD PARAMETERS

Complex		Band position (cm⁻¹)	Assignment	*Dq* (cm⁻¹)	*B* (cm⁻¹)	β	ν_2/ν_1
$Co(Htot)_2(H_2O)_2$	ν_1	9030	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$				
	ν_2 (exp.)	19085	${}^4T_{1g}(F)\rightarrow{}^4A_{2g}$	1014	1090	0·95	2·1
	ν_2 (calc.)	19080					
	ν_3	24100	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}(P)$				
$Co(Htot)_2(ampy)(H_2O)_2$	ν_1	9524	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$				
	ν_2 (exp.)	20495	${}^4T_{1g}(F)\rightarrow{}^4A_{2g}$	1096	1096	0·95	2·14
	ν_2 (calc.)	20495					
	ν_3	24400	${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$				
$Co(tot)(ani)(H_2O)$	ν_1	9710	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$				
	ν_2 (exp.)	21362	${}^4T_{1g}(F)\rightarrow{}^4A_{2g}$	1120	971	0·85	2·19
	ν_2 (calc.)	21362					
	ν_3	22724	${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$				
$Co(tot)(NH_3)(H_2O)_3$	ν_1	9710 (6)	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$				
	ν_2 (exp.)	20250 (5)	${}^4T_{1g}(F)\rightarrow{}^4A_{2g}$	1080	1084	0·95	2·18
	ν_2 (calc.)	20252					
	ν_3	24100 (46)	${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$				
$Co(tot)(quin)(H_2O)$	ν_1	8550	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$				
	ν_2 (exp.)	18630	${}^4T_{1g}(F)\rightarrow{}^4A_{2g}$	941	855	0·82	2·195
	ν_2 (calc.)	18810					
	ν_3	20410	${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$				
$Co(tot)(tea)(H_2O)_4$	ν_1	9700 (7)	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$				
	ν_2 (exp.)	20000 (8)	${}^4T_{1g}(F)\rightarrow{}^4A_{2g}$	1080	1084	0·95	2·06
	ν_2 (calc.)	20250					
	ν_3	24100 (52)	${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$				
$Co(tot)(Py)_2(H_2O)_2$	ν_1	8621 (9)	${}^4T_{1g}(F)\rightarrow{}^4T_{2g}$				
	ν_2 (exp)	19050 (7)	${}^4T_{1g}(F)\rightarrow{}^4A_{2g}$	1008	900	0·79	2·2
	ν_2 (calc.)	19200					
	ν_3	20833 (56)	${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$				
$Fe(Htot)_2(H_2O)_4$	ν_1	10500 9000 (shoulder)	${}^5T_{2g}\rightarrow{}^5E_g$	1050	—	—	—

The values in parentheses are the extinction coefficient values calculated in the case of soluble complex only.

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*Band positions in cm⁻¹.

metal ion (*A*-class of metal ion) which preferentially binds with oxygen and nitrogen donor atoms.

Iron complex — In octahedral high-spin Fe(II) complex one should expect a band ($^5T_{2g}\rightarrow{}^5E_g$) around 10000, while in tetrahedral complex a band ($^5E_g\rightarrow{}^5T_{2g}$) should appear around 4000. The presence of a band at 10500 in the present iron complex indicates the octahedral geometry of the complex which is also in conformity with the magnetic moment data. The value of 10 *Dq* calculated from the position of this band is similar to the ones obtained for Ni(II) and Co(II) complexes with the same ligand.

The band at 10500 appeared to be split into two components. This may be explained either by the presence of low ligand field component or by the John-Teller distortion.

Generally, Fe(II) complexes exhibit M→L charge-transfer bands[20]. A very intense band around 20,000 in the spectrum of the present complex may be due to charge-transfer.

Pd(IV), Pt(IV) and Rh(III) complexes — In the spectra of these complexes, only very intense bands appear in the visible region. These may be assigned to charge-transfer bands which will mask the weak *d-d* transitions of the complexes. So, no definite assignments of the geometries could be made on the basis of the spectral data. However, the diamagnetism of the complexes indicate their octahedral geometries which conform to the preferred geometries which these metal ions generally take in their complexes.

Infrared Spectra

The IR spectra of the ligand, its sodium and ammonium salts have been discussed earlier[1]. It has been indicated that the predominant tautomeric form of the ligand present in the solid state is the thione form.

The ligand molecule contains —COOH, —NH—C=S, and —NH—C=O groups and shifts in the spectra of the complexes should be expected in the positions of the bands due to these groups. It is reasonable to expect similar shifts in the band positions of complexes having the same bonding pattern. The complexes have been, therefore, classified into the following groups based on the directions of the shifts in the major infrared band positions. The infrared spectra of their deuterated forms have also been studied in order to confirm the band assignments.

Complexes of the type $ML_2(H_2O)_x(X)_y$ *[where M= Co(II), Fe(II)]* — The shifts in the band positions in the infrared spectra of $CoL_2(H_2O)_2$, $FeL_2(H_2O)_4$, and $CoL_2(ampy)(H_2O)_2$ were similar to those of $NiL_2(H_2O)_2$, the spectrum of which has been discussed in our earlier communication[1]. In the case of $CoL_2(ampy)(H_2O)_2$, bands due to aminopyridine were also present besides those due to $CoL_2(H_2O)_2$ moiety. It is, therefore, assumed that the bonding sites in these complexes are carbonyl and carboxyl oxygen atoms besides aminopyridine and water molecules.

Complexes of the type $CoL(H_2O)_a(X)_b$ — The shifts of the band positions in these complexes were similar to those in the spectra of $NiL(H_2O)_a(X)_b$ and Cu(II) complexes[1]. It is, therefore, assumed that the bonding sites are carboxylate oxygen, ring nitrogen of the NH group (after deprotonation) and amine and water molecule.

Platinum and palladium complexes — The bands in the spectra of the platinum and palladium complexes were rather broad which may be due to their polymeric nature. However, the following shifts were observed in some of the band positions: (i) The position of the band at 1740 due to carboxylate COO shifted to 1700. (ii) The positions of the bands at 1680, 680 and 620 did not change suggesting no interaction with carbonyl or amide group. (iii) The positions of the thioamide bands at 1030 and 945 shifted to 1000 and 900 respectively. (iv) The intensities of the νN-H and νN-D were relatively smaller than those in the ligand and deuterated ligand respectively. In the spectrum of the complex, a very broad band at 3000 appeared. The broadness of the band may be due to hydrogen bonding. (v) Two new bands appeared around 470 and 320. These have been assigned to νM-O and νM-S. (vi) The band at 1230 shifted to 1270 and another weak band appeared at 1220.

From the above shifts the bonding of the metal ion through the oxygen of carboxylate group, nitrogen of one of the N-H groups (after deprotonation) and thiocarbonyl sulphur atoms has been suggested.

Rhodium complex, $RhL_2(H_2O)_2$ — The IR spectrum of rhodium complex is similar to that of Pt(IV) complex except for the following differences:

(i) The band positions due to ν O-H, νN-H and νC-H at 3500, 3200 and 3160 respectively were shifted on duteration to 2450, 3200, and 3160. It appears that in this complex, only the water molecules are exchanged by D_2O while the protons of the N-H and C-H are not exchanged. This is further confirmed by the fact that the positions of the bands due to δN-H, and τN-H at 1550, 1440, and 720 did not shift on deuteration while that of δO-H of water molecule shifted to 1090.

(ii) The bands due to νC=S at 940 and 1020 splitted into two bands each at 935 and 920 and 1020 and 1010 respectively. It appears that there are two types of C=S groups in the complex, one bonded to metal ion resulting in the lowering of C=S band positions and a non-bonded C=S, in which case the positions of the bands will not shift.

(iii) All the bands due to coordinated water molecules are present at 3500, 1600 and 850.

(iv) The shifts in bands due to N-H groups were rather confusing. Some bands were shifted towards higher wave number side while the others remained unchanged. In order to keep the charge balance, one of the N-H groups of the ligand has to be deprotnated to coordinate with the metal ion and thus, it will complicate the spectrum.

(v) Two new bands at 550 and 370 appeared in the spectrum of the complex. These have been assigned to νM-O and νM-S respectively.

Hence the bonding through oxygen of carboxylate group and N of one of the N-H groups (deprotonated), thiocarbonyl sulphur and two molecules of water has been proposed.

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