

Synthesis and spectral studies of ternary complexes of Ni(II) and dioxouranium(VI) with 2-hydroxy-1-naphthaldehyde and some amino acids

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The 1:1:1 ternary complexes of Ni(II) and dioxouranium(VI) with 2-hydroxy-1-naphthaldehyde (A') and some amino acids have been synthesized and characterized. The IR spectral data of the complexes indicate that histidine, aspartic acid and glutamic acid act as tridentate ligands while glycine, α -alanine, β -alanine, valine, leucine, phenylalanine, serine and threonine act as bidentate ligands coordinating through amino nitrogen and carboxylic oxygen. The electronic spectra of the nickel(II) complexes suggest that they are octahedral. An eight coordination has been proposed for uranyl complexes also.

In continuation of our earlier work on mixed ligand complexes of dioxouranium¹ and copper², we report here the synthesis and characterization of mixed ligand complexes of nickel(II) and dioxouranium(VI) with 2-hydroxy-1-naphthaldehyde (A') and some amino acids like glycine (gly), DL- α -alanine (α -ala), DL- β -alanine (β -ala), L-valine (val), L-leucine (leu), DL-phenylalanine (O-ala), DL-serine (ser), DL-threonine (threo), L-histidine (hist), L-aspartic acid (asp), and L-glutamic acid (glut). The complexes have been characterised on the basis of analytical, conductivity, thermal, magnetic, infrared and electronic spectral data.

Experimental

The ligand 2-hydroxy-1-naphthaldehyde was obtained from the Sigma Chemical Company (USA) and α -amino acids were obtained from Loba Chemical Company. These were recrystallised before use and their purity was checked by TLC and melting point determination.

The following general procedure was adopted for the synthesis of the ternary complexes.

A solution of 2-hydroxy-1-naphthaldehyde (0.02 mol) was prepared in minimum amount of methanol. The amino acids (0.02 mol) were dissolved in water. The two solutions were simultaneously added to a methanolic solution of nickel chloride or uranyl acetate (0.01 mol) with constant stirring. The pH of the re-

sulting solution was adjusted to 5-6 by adding sodium acetate. The reaction mixture was refluxed on a water bath for 30 min. On cooling the reaction mixture, the solid complex separated out, which was filtered, washed with hot water and methanol to remove the excess ligand and the metal ion. The complexes obtained were dried *in vacuo* over fused anhydrous calcium chloride.

The analytical data (C, H and N) for the solid complexes were obtained from the Micro Analytical Laboratory, Calcutta University, Calcutta. The metal content in the complexes were determined as dimethyl glyoximate in case of nickel³ and by the oxinate method in the case of uranyl ion⁴. The conductivity measurements were made in DMF using a Digital conductivity bridge model 304. The magnetic susceptibility measurements were made at room temperature by the Gouy method using Hg[Co(NCS)₄] as the calibrant. Diamagnetic corrections were made using Pascal's constants. The thermal data of the complexes were obtained using a Stanton thermobalance. The infrared spectra of the ligands and complexes (4000-200 cm⁻¹) were recorded on a Perkin-Elmer infrared spectrophotometer model-283 using KBr pellets. The electronic spectra of the complexes were recorded in DMF on a Shimadzu multipurpose spectrophotometer model MPS-5000.

Results and discussion

The characterization data of the complexes are presented in Table 1. The complexes are insoluble in water and common solvents but freely soluble in DMF and DMSO. Except for the aspartic and glutamic acid complexes, others are non-electrolytic in nature. The molar conductance values in case of aspartic acid and glutamic acid complexes are in the range of 40-60 ohm⁻¹cm²mol⁻¹ suggesting that they are 1:1 electrolytes⁵. All the complexes have an endothermic peak in the DTA curve in the temperature range 160-190°C showing the presence of coordinated water⁶. The TGA curves of the above complexes show a mass loss corresponding to two water molecules in complexes 1-8, and one water molecule in 9-11 complexes in the temperature range 150-200°C.

Infrared spectra

The IR spectrum of 2-hydroxy-1-naphthaldehyde contains two characteristic bands at 3360 and 1725 cm⁻¹, due to phenolic ν OH and aldehyde ν C=O respectively. The disappearance of the former band and a negative shift in the latter band ($\Delta\nu = 15-40$ cm⁻¹) in

Table 1—Characterisation data of the ternary complexes

Complex	Decomp temp	Found (Calc), %				Magnetic moment (B.M.)
		M	C	H	N	
[NiA' gly.2H ₂ O]	250	16.93 (17.27)	45.43 (45.90)	4.28 (4.41)	3.86 (4.12)	3.12 (3.17)
[NiA' α-ala.2H ₂ O]	260	16.02 (16.60)	47.38 (47.50)	4.60 (4.81)	3.60 (3.96)	3.14 (3.16)
[NiA' β-ala.2H ₂ O]	270	16.28 (16.60)	47.24 (47.50)	4.67 (4.81)	3.52 (3.96)	3.21 (3.27)
[NiA' val.2H ₂ O]	265	15.11 (15.38)	50.16 (50.31)	5.35 (5.50)	3.43 (3.67)	3.26 (3.23)
[NiA' leu.2H ₂ O]	255	14.13 (14.84)	51.19 (51.55)	5.44 (5.81)	3.19 (3.54)	3.18 (3.13)
[NiA' φ-ala.2H ₂ O]	255	12.67 (13.29)	56.82 (57.05)	4.33 (4.75)	2.98 (3.17)	3.19 (3.21)
[NiA' ser.2H ₂ O]	265	15.35 (15.88)	45.13 (45.44)	4.38 (4.60)	3.50 (3.79)	3.14 (3.19)
[NiA' threo.2H ₂ O]	260	14.67 (15.30)	46.67 (46.91)	4.49 (4.95)	3.16 (3.45)	3.16 (3.20)
[NiA' hist.H ₂ O]	250	14.72 (14.61)	49.21 (50.78)	3.83 (4.23)	10.34 (10.46)	3.20 (3.21)
H[NiA' asp.H ₂ O]	265	15.11 (15.50)	47.26 (47.53)	3.46 (3.70)	3.37 (3.70)	3.12 (3.14)
H[NiA' glut.H ₂ O]	255	14.49 (14.91)	48.48 (48.77)	3.91 (4.32)	3.41 (3.56)	3.19 (3.16)
[UO ₂ A' gly.2H ₂ O]	265	48.73 (49.00)	28.06 (28.31)	3.71 (3.72)	2.56 (2.54)	23
[UO ₂ A' α-ala.2H ₂ O]	258	41.69 (42.12)	28.13 (29.74)	2.94 (3.01)	2.32 (2.48)	17
[UO ₂ A' β-ala.2H ₂ O]	263	41.73 (42.12)	29.22 (29.74)	3.33 (3.01)	2.52 (2.48)	15
[UO ₂ A' val.2H ₂ O]	267	39.62 (40.14)	31.94 (32.38)	3.17 (3.54)	2.21 (2.36)	19
[UO ₂ A' leu.2H ₂ O]	273	38.75 (39.21)	33.27 (33.61)	3.86 (3.79)	2.18 (2.31)	15
[UO ₂ A' φ-ala.2H ₂ O]	256	38.11 (39.95)	38.82 (39.28)	3.48 (3.44)	1.95 (2.29)	21
[UO ₂ A' ser.2H ₂ O]	265	41.04 (41.90)	28.89 (29.58)	2.79 (2.82)	2.19 (2.47)	19
[UO ₂ A' threo.2H ₂ O]	269	39.27 (40.00)	29.98 (30.25)	3.05 (3.19)	2.07 (2.35)	12
[UO ₂ A' hist.H ₂ O]	253	43.88 (44.05)	32.95 (33.28)	2.58 (2.77)	6.76 (6.85)	20
H[UO ₂ A' asp H ₂ O]	261	40.13 (40.34)	30.29 (30.51)	2.16 (2.37)	2.19 (2.37)	49
H[UO ₂ A' gluta H ₂ O]	274	38.94 (39.30)	31.53 (31.74)	2.64 (2.81)	2.08 (2.31)	62

the nickel(II) and dioxouranium(VI) complexes suggest the involvement of phenolic and carbonyl oxygen atoms in coordination with the metal ion. The free amino acids exhibit bands⁷⁻⁹ around 3265, 3120 and 1515 cm⁻¹ which may be assigned to $\nu_{as}(\text{NH}_2)$,

$\nu_s(\text{NH}_2)$ and $\delta(\text{NH}_2)$. These bands are shifted to lower frequency region ($\Delta\nu = 40-70 \text{ cm}^{-1}$) in the complexes indicating the involvement of amino nitrogen in coordination. The bands due to $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ of carboxylic group are observed in the re-

Table 2—Electronic spectral data and log ϵ of ligand field parameters of Nickel(II) complexes

Complex	$\nu_1(\text{cm}^{-1})$ (log ϵ)	$\nu_2(\text{cm}^{-1})$ (log ϵ)	$\nu_3(\text{cm}^{-1})$ (log ϵ)
[NiA' gly.2H ₂ O]	9302 2.60	15576 2.70	27027 2.58
[NiA' α -ala.2H ₂ O]	9345 2.45	15625 2.57	27174 2.56
[NiA' β -ala.2H ₂ O]	9756 2.58	15625 2.62	26882 2.53
[NiA' val.2H ₂ O]	9569 2.53	15503 2.58	26810 2.49
[NiA' leu.2H ₂ O]	9216 2.42	15625 2.59	26951 2.51
[NiA' ϕ -ala.2H ₂ O]	9523 2.45	16000 2.58	27100 2.34
[NiA' ser.2H ₂ O]	9433 2.42	15503 2.62	26809 2.46
[NiA' Threo.2H ₂ O]	9478 2.49	15503 2.54	27026 2.26
[NiA' hist. H ₂ O]	9524* 2.38	15873 2.58	26882 2.39
H[NiA' asp. H ₂ O]	9259 2.28	15748 2.51	26667 2.38
H[NiA' glut.H ₂ O]	9345 2.32	15625 2.56	26596 2.34

gion of 1630-1600 and 1420-1400 in the free ligands. A bathochromatic shift of these bands to the extent of 25-40 and 30-40 cm^{-1} respectively is observed in the complexes, suggesting the coordination of oxygen with metal ion. The absence of $\nu(\text{O}-\text{H})$ of the carboxylic group appearing at 2600 cm^{-1} in free ligands, confirms the deprotonation of COOH group and participation of oxygen in coordination¹⁰.

The appearance of a broad band centred at 2800 cm^{-1} in the serine and threonine complexes, may be due to the stretching mode of hydrogen bonded hydroxyl group (with NH₂). This indicates non-participation of hydroxyl group of these ligands. Thus the ligands are acting as bidentate coordinating through amino nitrogen and carboxylic oxygen only. However, in the histidine complexes, a lowering in the characteristic bands of the amino group to an extent of 30-40 cm^{-1} is observed, indicating tridentate coordination of histidine.

The characteristic bands of the coordinated water are observed in all the complexes around 3600-3200,

1630-1600 and 800-700 cm^{-1} due to $\nu(\text{HOH})$, $\delta(\text{HOH})$ and $\rho_r(\text{HOH})$ respectively¹¹. The stretching vibrations $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ are observed around 500 and 400 cm^{-1} respectively¹²⁻¹⁴. The bands observed at 920-910, 830-820 and 250-240 cm^{-1} may be assigned to $\nu_{\text{as}}(\text{O}-\text{U}-\text{O})$, $\nu_{\text{s}}(\text{O}-\text{U}-\text{O})$ and $\delta(\text{O}-\text{U}-\text{O})$ modes respectively of linear UO_2 ion^{15,16}.

All the nickel complexes show three peaks in the range 9200-9700, 15500-16000 and 25100-27200 cm^{-1} (Table 2). These bands are expected for an octahedral geometry^{17,18} and have been assigned to the transitions, ${}^3T_{2g}(\text{F}) \rightarrow {}^3A_{2g}(\text{F})$ (ν_1), ${}^3T_{1g}(\text{F}) \rightarrow {}^3A_{2g}(\text{F})$ (ν_2) and ${}^3T_{1g}(\text{P}) \rightarrow {}^3A_{2g}(\text{F})$ (ν_3).

The magnetic moments of the Ni(II) complexes correspond to two unpaired electrons (Table 1). This is consistent with pseudo-octahedral geometry.

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References

- Mrudula Rao B V, Swamy S J, Lingaiah P, *Indian J Chem*, 24A (1985) 887.
- Mrudula Rao B V, Venkatanarayana G Lingaiah P, *Indian J Chem*, 27A (1988) 261.
- Vogel A I, *A text book of quantitative inorganic analysis*, 3rd Edn (Longman, London) 1961, 429.
- Flaschka H, *Mikrochim Acta*, 55 (1955).
- Geary W J, *Coord chem Rev*, 7 (1971) 81.
- Nikolaev A V, Myachina L T, Logvinenko V A, *Thermal analysis*, Vol 2 (Academic Press, New York), 1969, 779.
- Tsuboi M, Onishi K, Nakagawa I, Shimanouchi T Mizushima S, *Spectrochim Acta*, 12 (1958) 253.
- Fukushima K, Onishi K, Shimanouchi T Mizushima S, *Spectrochim Acta*, 14 (1959) 236.
- Sen D N, Mizushima S, Kurran C Quagliano J V, *J Am chem Soc*, 77 (1955) 211.
- Young R P, *J Heterocyclic Chem*, 9 (1972) 371.
- Nakamoto K, *Infrared and Raman spectra of inorganic and compounds* (Wiley, New York), 1978, 227.
- Adams D M, *Metal ligand and related vibrations* (Ernold, London) 1967.
- Prabhakaran C P, Patel C C, *J inorg nucl Chem*, 37 (1975) 1901.
- Djordjevic C, *Spectrochim Acta*, 17 (1961) 448.
- Cattalina L, Cratto U, Degetto S Tondello E, *Inorg chim Acta Rev*, 5 (1971) 19.
- Galkin N P, Karpov V I, Beiryatin V D, *Russ J Inorg Chem*, 7 (1962) 1043.
- Lever A B P, *Inorganic electronic spectroscopy* (Elsevier, Amsterdam) 1968.
- Sacconi L, *Trans Met Chem*, 4 (1968) 199.