

Synthesis and Spectral Studies of Dioxouranium(VI) Complexes of Amide Group Containing Ligands

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A new series of complexes of dioxouranium(VI) complexes with 2-(acetyl amino) benzoic acid, 2-(benzoylamino) benzoic acid, 2-(2-aminobenzoylamino) benzoic acid, 2-(aminobenzanilide) 2-(aminocarbonyl) benzoic acid, 2-[(2-aminophenylamino)-carbonyl] benzoic acid, maleanilic acid, malea-1-naphthanilic acid, 2-[(phenylamino) carbonyl] benzoic acid and 2-[(2-naphthalenylamino) carbonyl] benzoic acid have been synthesised and characterized by physico-chemical data.

INTRODUCTION

Amide group containing ligands are biologically potent and there are numerous examples of *in vivo* interactions of transition metal ions with these ligand system^{1,2}. In continuation of our earlier work on the transition metal complexes of amide group containing ligands³⁻⁷, we report here the synthesis of dioxouranium(VI) complexes of 2-(acetyl amino) benzoic acid (AABA), 2-(benzoylamino) benzoic acid (BABA), 2-(2-aminobenzoylamino) benzoic acid (ABABA), 2-(amino benzanilide) (ABn), 2-(aminocarbonyl) benzoic acid (ACBA), 2-[(2-aminophenylamino) carbonyl]-benzoic acid (APCBA), maleanilic acid (MA), malea-1-naphthanilic acid (MMA), 2-[(phenylamino) carbonyl] benzoic acid (PACBA) and 2-[2-naphthalenylamino) carbonyl] benzoic acid (NACBA) and their characterization based on analytical, conductance, thermal, magnetic and infrared and electronic spectral data.

EXPERIMENTAL

All the chemicals used were of AR grade. AABA, BABA, ABABA, ABn, ACBA, APCBA, MA, MNA, PACBA and NACBA were prepared by literature methods⁸.

The complexes were prepared by mixing a solution of uranyl acetate dihydrate (0.02 mol) with methanolic solution of the ligands (0.04 mol) and heating the mixture on a hot water bath for about 30-60 min. The crystalline complexes formed were suction filtered, washed with hot water and methanol and dried *in vacuo* over anhydrous CaCl₂.

The UO₂ (VI) complexes were analysed for C, H and N at the Microanalytical Laboratory, Calcutta University, Calcutta, India. The conductance of the com-

plexes in DMF at the concentration 10^{-3} M was measured using a Digisun Digital Conductivity Meter, Model DI 909. The thermal data of the complexes were obtained employing Stanton thermobalance available at Indian Institute of Chemical Technology, Hyderabad. The IR spectra of the ligands and the metal complexes ($4000-200\text{ cm}^{-1}$) in Nujol mulls and in KBr pellets (using CsI plates in far infrared region) were recorded on a Perkin-Elmer 283 spectrophotometer. The electronic spectra of the complexes in DMF were obtained with Shimadzu MPS 5000 spectrometer.

RESULTS AND DISCUSSION

All the complexes are stable at room temperature and are non-hygroscopic. They are slightly soluble in methanol and freely soluble in DMF and DMSO.

The analytical, thermal, conductance and magnetic data obtained for the UO_2 (VI) complexes are presented in Table-1. It is clear from the table that the experimental values are in good agreement with the calculated ones for the composition given for each of them. All the complexes except those of ABABA, APCBA show initial weight loss in the temperature range $140-220^\circ\text{C}$ corresponding to loss of two water molecules. The expulsion of water molecules in the above range of temperatures indicates that they are coordinated⁹. The presence of water

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF UO_2 (VI) COMPLEXES

Complex (Colour)	Decomposition Temp. ($^\circ\text{C}$)	Found (Calcd.) %			Λ_m (ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$)
		N	C	H	
$[\text{UO}_2(\text{AABA})_2(\text{H}_2\text{O})_2]$ Yellow	265	4.20 (4.21)	32.50 (32.53)	3.00 (3.01)	12.0
$[\text{UO}_2(\text{ABABA})_2]$ Light yellow	270	7.10 (7.14)	42.80 (42.85)	2.90 (2.93)	13.0
$[\text{UO}_2(\text{ACBA})_2(\text{H}_2\text{O})_2]$ Orange yellow	255	4.35 (4.40)	30.15 (30.18)	2.50 (2.51)	14.0
$[\text{UO}_2(\text{BABA})_2(\text{H}_2\text{O})_2]$ Light Yellow	260	3.50 (3.56)	42.71 (42.74)	3.07 (3.05)	12.5
$[\text{UO}_2(\text{Abn})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{COO}_2)]$ Light Yellow	270	7.62 (7.67)	42.70 (42.73)	3.80 (3.83)	125.0
$[\text{UO}_2(\text{APCBA})_2]$ Yellow	280	7.09 (7.14)	42.79 (42.85)	2.89 (2.98)	10.5
$[\text{UO}_2(\text{MA})_2(\text{H}_2\text{O})_2]$ Yellow	270	4.00 (4.05)	34.75 (35.78)	3.45 (3.47)	10.0
$[\text{UO}_2(\text{MNA})_2(\text{H}_2\text{O})_2]$ Light Yellow	260	3.53 (3.56)	42.72 (42.74)	3.62 (3.65)	12.5
$[\text{UO}_2(\text{PACBA})_2(\text{H}_2\text{O})_2]$ Yellow	267	3.52 (3.56)	42.70 (42.74)	3.00 (3.05)	11.0
$[\text{UO}_2(\text{NACBA})_2(\text{H}_2\text{O})_2]$ Yellow	270	3.13 (3.16)	48.72 (48.75)	3.15 (3.16)	13.5

molecules in these complexes is further evidenced by their DTA curves which give endothermic peak in the temperature range 150–250°C. The ligands under study form complexes of varying thermal stability and the order may be as: ACBA < BABA < MNA < AABA < PACBA < ABABA ≈ NACBA ≈ ABn ≈ MA < APCBA. All the UO₂(VI) complexes, except that with ABn show only residual molar conductance values (10–14 mhos cm² mol⁻¹) suggesting that they are non-electrolytes. The complexes of ABn exhibits a value of 125 mhos cm² mol⁻¹ corresponding to 1 : 2 electrolyte.

The infrared spectra of all the ligands show a bond at 2600 cm⁻¹ which is assigned to $\nu(\text{O—H})$ of carboxylic group. The strong bands at 1700 and 1330 cm⁻¹ due to $\nu(\text{C=O})$ and $\nu(\text{C—OH})$ stretching modes respectively in the ligands^{10,11} disappear in the complexes and are replaced by two bands around 1550 and 1380 cm⁻¹ due to $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ vibrations respectively¹². The $\nu(\text{N—H})$ frequency appearing at 3460 and 3380 cm⁻¹ in AABA and BABA respectively undergoes a negative shift in their complexes by 160–180 cm⁻¹ indicating that nitrogen of the amide group is coordinating¹¹. A band around 1640 cm⁻¹ in the ligands assignable to $\nu(\text{C=O})$ vibration of amide remains almost unchanged in the complexes thus ruling out coordination through amide oxygen.

In PACBA and NACBA complexes the $\nu(\text{NH})$ frequency shifts towards higher region as compared to its position in the spectra of the ligands indicating non-participation of nitrogen atom in coordination¹³. This behaviour of nitrogen can be accounted for by the presence of bulky phenyl or naphthyl group attached to it which hinders the coordination of nitrogen. The $\nu(\text{C=O})$ frequency of these ligands (around 1650 cm⁻¹) undergoes a negative shift by 30 cm⁻¹ in the complexes indicating coordination of this group through oxygen. Further, the participation of the nitrogen and oxygen atoms in coordination is supported by the bands in far infrared spectra around 500 and 400 cm⁻¹ respectively which may be assigned to $\nu(\text{U—N})$ and $\nu(\text{U—O})$ ^{14,15}. In all the complexes, a broad band is observed at 3590 cm⁻¹ due to $\nu(\text{OH})$ of coordinated water and a broad band at 375 cm⁻¹ due to $\nu(\text{M—OH})$ mode¹⁶. The bands at 910–900, 830–820 and 250–240 cm⁻¹ are observed in all the complexes and these may be assigned to $\nu_{\text{asym}}(\text{O—U—O})$, $\nu_{\text{sym}}(\text{O—U—O})$ and $\delta(\text{O—U—O})$ modes respectively of uranyl ion indicating the linear form of UO₂(VI) ion^{17,18}.

Thus, it may be concluded that AABA, BABA, ACBA, MA, MNA, PACBA and NACBA act as mononegative, bidentate ligands, the first two coordinating through carboxylate oxygen and amide nitrogen and the remaining through carboxylate oxygen and amide oxygen. ABABA and APCBA are mononegative tridentate bonding through carboxylate oxygen and amine nitrogen and the former additionally through amide nitrogen and the latter through amide oxygen. ABn functions as a neutral bidentate ligand coordinating through amide oxygen and amine nitrogen.

The magnetic studies made on the complexes indicate that they are diamagnetic in nature.

The UV spectra of uranyl complexes exhibit a strong band in the 21000–22500 cm⁻¹ region¹⁹ which is assigned to the transition $3u \leftarrow {}^1E_g$ ²⁰. However, it

has not been possible to assign several other bands observed beyond 25000 cm^{-1} in the spectra of the complexes.

Thus, based on all the data obtained six coordination is proposed around UO_2 (VI).

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REFERENCES

1. K.N. Raymond and C.J. Carrano, *Acc. Chem. Res.*, **12**, 183 (1979).
2. H. Sigel and R.B. Martin, *Chem. Rev.*, **82**, 385 (1982).
3. V. Ravindar, S. Jagannatha Swamy, S. Srihari and P. Lingaiah, *Trans. Met. Chem.*, **9**, 103 (1984).
4. G. Dayakar, G. Balaswamy, V. Ravindar and P. Lingaiah, *Trans. Met. Chem.*, **12**, 539 (1987).
5. G. Dayakar and P. Lingaiah, *Trans. Met. Chem.*, **14**, 203 (1989).
6. _____, *Indian J. Chem.*, **35A**, 614 (1996).
7. _____, *Asian J. Chem.*, **9**, 179 (1997).
8. V. Ravindar, S.J. Swamy, S. Srihari and P. Lingaiah, *Polyhedron*, **4**, 1511 (1985).
9. A.V. Nikolaev, V.A. Longvinenko and C.I. Myachina, *Thermal Analysis*, Academic Press, New York, Vol. p. 779 (1969).
10. R.P. Young, *J. Hetero Chem.* **9**, 371 (1972).
11. D. Hazdi and M. Pintar, *Spectrochim. Acta*, **8**, 249 (1959).
12. B. Singh, V. Banerjee, B.V. Agarwala and K.D. Aruna, *J. Indian Chem. Soc.*, **57**, 365 (1980).
13. B.S. Pannu and L.S. Chopra, *J. Indian Chem. Soc.*, **51**, 387 (1974).
14. D.M. Adams, *Metal Ligand and Related Vibrations*, Arnold, London (1967).
15. G.T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).
16. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1978).
17. L. Marchi and Reynolds, *J. Am. Chem. Soc.*, **65**, 333 (1943).
18. N.P. Galkin, V.I. Karpov and V.D. Veryatin, *Russ. J. Inorg. Chem.*, **7**, 1043 (1962).
19. A.M. Shallaby, M.M. Mostfe, K.M. Ibrahim and M.N.H. Moussa, *Spectrochim. Acta*, **40**, 999 (1984).
20. S.P. McGlynn and J.K. Smith, *Symposium in Molecular Electronic Spectroscopy*, *J. Mol. Spectro*, **6**, 164, 188 (1961).

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