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# Uranyl Nitrate Complexes of some Schiff Bases of 4-Aminoantipyrine and Certain Carbonyl Compounds

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## Abstract

A series of nine complexes of uranyl nitrate with some Schiff bases derived from 4-aminoantipyrine and certain carbonyl compounds, such as benzaldehyde, 2-nitrobenzaldehyde, 3-nitrobenzaldehyde, 4-methylbenzaldehyde, 4-*N,N*-dimethylaminobenzaldehyde, 2-hydroxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, acetylacetone and benzoylacetone have been synthesized. These complexes have been characterized by elemental analysis, molecular weight determination and IR spectral, conductance and magnetic studies. From these studies they can be formulated as $[UO_2L_2(NO_3)_2]$, in which the first five ligands (in the order given above) and nitrate ions are coordinated bidentately, while the last four ligands (which have either a phenolic hydroxyl group or a side-chain carbonyl group as an additional site) act as terdentate ligands, and nitrate ions are coordinated monodentately. Hence the proposed general formula for the complexes suggests that the uranyl ion has a coordination number of eight in addition to the two oxygen atoms which have already been bonded to the U(VI) species.

## Introduction

The uranyl ion, $UO_2^{2+}$, is significant due to its unusual solubility in organic layers and also due to its easy extractability from aqueous layers. It has little or no ionization and the nitrate ions are coordinated in the equatorial plane of the $UO_2$ system [1]. Among the complexes of uranium, U(VI) complexes have been the most extensively studied, all of which are derived from the oxycation, $UO_2^{2+}$. A search through the literature has revealed that the 4-aminoantipyrine complex of uranyl nitrate has been synthesized recently [2]. We thought it would be interesting to prepare some Schiff bases of 4-aminoantipyrine with certain carbonyl compounds and to synthesize their uranyl nitrate complexes. For this purpose the following nine Schiff bases of 4-aminoantipyrine have been prepared using the respective carbonyl compounds (these Schiff bases are abbreviated as those given in parentheses): 4*N*-(benzylidene)aminoantipyrine (BAAP), 4*N*-(2′-nitrobenzylidene)aminoantipyrine (*o*-NBAAP), 4*N*-(3′-nitrobenzylidene)aminoantipyrine (*m*-NBAAP), 4*N*-(4′-methylbenzylidene)aminoantipyrine (MBAAP), 4*N*-(4′-*N,N*-dimethylaminobenzylidene)aminoantipyrine (ABAAP), 4*N*-(2′-hydroxybenzylidene)aminoantipyrine (HBAAP), 4*N*-(2′-hydroxy-1′-naphthylidene)-aminoantipyrine (HNAAP), 4*N*-(acetylisopropylidene)aminoantipyrine (AIPAAP) and 4*N*-(benzoylisopropylidene)aminoantipyrine (BIPAAP).

## Experimental

Uranyl nitrate (BDH AnalaR, 99.9% pure) was used as such. The nine Schiff bases listed above were prepared by the general method, in which equimolar amounts of 4-aminoantipyrine and the appropriate carbonyl compound in ethanol were mixed and refluxed for 2–3 h [3]. Yellow coloured crystals of these Schiff bases separated on cooling and were recrystallised from hot ethanol. The purities of these Schiff bases were checked by measuring their TLCs, IR spectra and melting points.

The complexes were prepared by the following methods.

(a) For the preparation of the uranyl complexes of BAAP, *o*-NBAAP, *m*-NBAAP or MBAAP, solutions of uranyl nitrate (2 mmol) and the ligand (4 mmol) in hot dry methanol were mixed and refluxed on a steam bath for 2–3 h. Then the reaction mixture was cooled to room temperature and crystals of the complex were formed, filtered, washed repeatedly with minimum amounts of hot methanol, and dried *in vacuo* over phosphorus(V) oxide.

(b) For the preparation of the complexes of ABAAP, HBAAP and BIPAAP, solutions of uranyl nitrate (2 mmol) and the ligand (4 mmol) in hot dry acetone were mixed and refluxed on a steam bath for about 2 h. After cooling, crystals of the complex were separated, filtered, washed several times

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with minimum amounts of hot acetone and dried *in vacuo* over phosphorus(V) oxide.

(c) The following method was employed for the preparation of the uranyl nitrate complex with AIPAAP. Solutions of uranyl nitrate (2 mmol) and AIPAAP (4 mmol) in hot ethanol were mixed and refluxed on a steam bath for about 5 h. Then the solution was concentrated to obtain a yellowish brown viscous mass, which was stirred several times with small amounts of hot benzene and the benzene layer was decanted each time to remove excess ligand. The solid mass thus obtained was dissolved in the minimum amount of hot ethanol and the complex was precipitated out by adding dry diethyl ether with vigorous stirring. The complex was filtered and dried *in vacuo* over phosphorus(V) oxide.

All the complexes were analysed for the metal contents by the conventional gravimetric method [4]. The carbon, hydrogen and nitrogen contents were analysed by the Central Drug Research Institute (Lucknow, India) on a payment basis. Molar conductivities of the complexes in acetonitrile and nitrobenzene ($\sim 10^{-3}$ M solutions) were measured at room temperature ($28 \pm 2$ °C) using an ELICO conductivity bridge CM82 with a dip-type cell (type cc-03) having platinum electrodes (cell constant, 1.33 $cm^{-1}$). Magnetic susceptibilities were measured also at room temperature by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. The IR spectra of the ligands (Schiff bases) and the complexes were recorded in the 400–4000 $cm^{-1}$ range on a Perkin Elmer 397 IR spectrophotometer using the KBr disc technique. The molecular weights of the complexes ($\sim 10^{-3}$ M solutions) were determined by the cryoscopic method using nitrobenzene as the solvent [5].

## Results and Discussion

Analytical data (Table I) of the complexes show that they have the composition $UO_2L_2(NO_3)_2$. All the complexes are pale yellow or orange–yellow coloured non-hygroscopic crystalline solids, which are moderately soluble to give dilute solutions (up to $\sim 10^{-2}$ mol) in acetone, acetonitrile, methanol, ethanol and chloroform, and are completely insoluble in benzene, carbon tetrachloride, diethyl ether and petroleum ether. The molar conductance values of the complexes in acetonitrile and nitrobenzene (Table I) indicate that all the complexes behave as non-electrolytes [6] and hence both the nitrate ions present in each of the complexes are also coordinated to the metal ion. All the complexes are found to be diamagnetic ($\mu_{eff} = 0$ BM) as expected for a $UO_2^{2+}$ system.

The important IR spectral bands of the ligands and the complexes are presented in Table II. The spectra of all the ligands except AIPAAP and BIPAAP have a strong band at 1640 $cm^{-1}$ which is attributed to the stretching vibration of the ring carbonyl group. The band corresponding to the ring carbonyl group in AIPAAP and BIPAAP appears at a lower region (1620 $cm^{-1}$), which may be due to the coupling effect of the vibrations of the side-chain carbonyl group with that of the ring carbonyl group present in them. The stretching vibration of the side-

TABLE I. Analytical[a], Molecular Weight[a] and Conductance[b] Data of Uranyl Nitrate Complexes with some Schiff Bases

| Complex | Metal (%) | Carbon (%) | Hydrogen (%) | Nitrogen (%) | Molecular weight | Molar conductance[b] | |
|---|---|---|---|---|---|---|---|
| | | | | | | Acetonitrile | Nitrobenzene |
| $[UO_2(BAAP)_2(NO_3)_2]$ | 24.08<br>(24.39) | 44.51<br>(44.26) | 3.67<br>(3.48) | 11.23<br>(11.48) | 925<br>(976) | 48.64 | 3.90 |
| $[UO_2(o\text{-}NBAAP)_2(NO_3)_2]$ | 22.13<br>(22.33) | 40.28<br>(40.53) | 3.37<br>(3.00) | 13.01<br>(13.13) | 1092<br>(1066) | 30.71 | 3.13 |
| $[UO_2(m\text{-}NBAAP)_2(NO_3)_2]$ | 22.24<br>(22.33) | 40.12<br>(40.53) | 3.56<br>(3.00) | 13.30<br>(13.13) | 1102<br>(1066) | 29.82 | 2.63 |
| $[UO_2(MBAAP)_2(NO_3)_2]$ | 23.62<br>(23.71) | 45.27<br>(45.42) | 3.92<br>(3.78) | 11.01<br>(11.16) | 1050<br>(1004) | 46.49 | 6.55 |
| $[UO_2(ABAAP)_2(NO_3)_2]$ | 22.37<br>(22.41) | 45.08<br>(45.20) | 4.25<br>(4.14) | 12.94<br>(13.18) | 1052<br>(1062) | 39.66 | 4.88 |
| $[UO_2(HBAAP)_2(NO_3)_2]$ | 23.42<br>(23.61) | 42.82<br>(42.86) | 3.39<br>(3.37) | 10.80<br>(11.11) | 1003<br>(1008) | 34.43 | 7.47 |
| $[UO_2(HNAAP)_2(NO_3)_2]$ | 21.56<br>(21.48) | 47.10<br>(47.65) | 3.92<br>(3.43) | 9.98<br>(10.11) | 1201<br>(1108) | 44.69 | 8.05 |
| $[UO_2(AIPAAP)_2(NO_3)_2]$ | 24.42<br>(24.69) | 45.08<br>(45.20) | 4.25<br>(4.14) | 12.94<br>(13.18) | 997<br>(964) | 62.93 | 7.75 |
| $[UO_2(BIPAAP)_2(NO_3)_2]$ | 21.58<br>(21.86) | 46.12<br>(46.32) | 3.95<br>(3.86) | 9.97<br>(10.29) | 1025<br>(1088) | 47.42 | 7.47 |

[a] Calculated values in parentheses. [b] $\sim 10^{-3}$ M solutions used; $ohm^{-1}$ $cm^2$ $mol^{-1}$.

TABLE II. Important IR Spectral Bands[a] (cm$^{-1}$) of some Schiff Bases and their Uranyl Nitrate Complexes

| Compound | $\nu_{OH}$ | $\nu_{C=O}$ (side chain) | $\nu_{C=O}$ (ring) | $\nu_{C=N}$ | $\nu_4(NO_3)$ | $\nu_1(NO_3)$ | $\nu_2(NO_3)$ | $\nu_3(O=U=O)$ |
|---|---|---|---|---|---|---|---|---|
| BAAP | | | 1640s | 1590s | 1510w | 1290s | 1030w | 925s |
| $[UO_2(BAAP)_2(NO_3)_2]$ | | | 1600m | 1560m | | | | |
| *o*-NBAAP | | | 1640s | 1590m | 1510w | 1290s | 1030w | 920s |
| $[UO_2(o\text{-}NBAAP)_2(NO_3)_2]$ | | | 1600m | 1560s | | | | |
| *m*-NBAAP | | | 1640s | 1590m | 1510m | 1290s | 1030w | 920s |
| $[UO_2(m\text{-}NBAAP)_2(NO_3)_2]$ | | | 1600w | 1560m | | | | |
| MBAAP | | | 1640s | 1590m | 1510w | 1290s | 1030s | 925s |
| $[UO_2(MBAAP)_2(NO_3)_2]$ | | | 1600s | 1560m | | | | |
| ABAAP | | | 1640s | 1590m | 1510w | 1280s | 1030m | 925s |
| $[UO_2(ABAAP)_2(NO_3)_2]$ | | | 1600s | 1560s | | | | |
| HBAAP | 3440br | | 1650s | 1590s | 1420w | 1290s | 1030m | 925s |
| $[UO_2(HBAAP)_2(NO_3)_2]$ | 3410br | | 1600s | 1560s | | | | |
| HNAAP | 3440br | | 1640s | 1590s | 1420w | 1290s | 1030m | 925s |
| $[UO_2(HNAAP)_2(NO_3)_2]$ | 3410br | | 1600m | 1540m | | | | |
| AIPAAP | | 1660s | 1620s | 1570s | 1460w | 1310w | 1025w | 920s |
| $UO_2(AIPAAP)_2(NO_3)_2]$ | | 1610m | 1610m | 1540w | | | | |
| BIPAAP | | 1660s | 1620s | 1570s | 1460sh | 1310w | 1025w | 935s |
| $[UO_2(BIPAAP)_2(NO_3)_2]$ | | 1610m | 1610m | 1540w | | | | |

[a] Abbreviations: s = strong, m = medium, w = weak, sh = shoulder, br = broad.

chain carbonyl group present in AIPAAP and BIPAAP appears at 1660 cm$^{-1}$. In the spectra of the complexes, all the carbonyl bands are shifted to a lower region (around 1600 cm$^{-1}$). For AIPAAP and BIPAAP there is only one strong band at 1610 cm$^{-1}$ in the spectra of their complexes, in spite of the fact that both of them have two carbonyl groups, one ring and one side-chain. These shifts (about 40–50 cm$^{-1}$) in the carbonyl vibrations indicate that all these ligands are coordinated to the metal ion through the carbonyl oxygen (for AIPAAP and BIPAAP both the carbonyl groups are coordinated).

The spectra of all the ligands have a strong band at 1590 cm$^{-1}$ (1570 cm$^{-1}$ for AIPAAP and BIPAAP due to the coupling effect of the closely lying carbonyl frequency) which is assigned to $\nu_{C=N}$. In the spectra of the complexes this band is shifted to 1560–40 cm$^{-1}$, indicating the coordination of the azomethine nitrogen to the metal ion. The ligands HBAAP and HNAAP have two bands at 3440 and 1310 cm$^{-1}$ which are assigned to the stretching vibrations of the phenolic OH and C–O bonds, respectively. In their complexes, however, these two bands are shifted correspondingly to 3410 ($\nu_{OH}$) and 1330 ($\nu_{C\text{–}O}$) cm$^{-1}$. These shifts indicate that the phenolic OH groups present in these two ligands are also coordinated to the metal ion. The higher frequency shift for the phenolic C–O bond on complexation is expected for the change from the hydrogen-bonded structure in the ligand to the covalent metal-bonded structure in the complex [7, 8].

In the spectra of the complexes, four additional bands are present. Of these, the band around 1030 cm$^{-1}$ is attributed to the $\nu_2$ vibration of the $NO_3$ group. The bands at 1510 and 1290 cm$^{-1}$ in the complexes of BAAP, *o*-NBAAP, *m*-NBAAP, MBAAP and ABAAP are the two split bands of the coordinated $NO_3$ ion. Since the magnitude of splitting is of the order of about 220 cm$^{-1}$ in these five complexes, the nitrate ions are coordinated bidentately in them [9]. In the remaining four complexes (namely, those of HBAAP, HNAAP, AIPAAP and BIPAAP) these split bands appear around 1460–20 cm$^{-1}$ and 1310–1290 cm$^{-1}$, respectively, and the magnitudes of splitting in these cases are in the range 150–130 cm$^{-1}$. This indicates that the nitrate ions are coordinated in a monodentate fashion in these four complexes [9]. The fourth additional band present in the spectra of all the complexes appears around 920 cm$^{-1}$ and is assigned to an asymmetric stretching vibration of O=U=O. Thus the coordination of the nitrate groups is confirmed by IR spectral (Table II) and conductance data (Table I).

Based on the above evidence and discussion, and in the absence of facilities for X-ray analysis, the present series of complexes have the following general formula: $[UO_2L_2(NO_3)_2]$. The ligands BAAP, *o*-NBAAP, *m*-NBAAP, MBAAP and ABAAP act as neutral bidentate ligands in these complexes, coordinating through the oxygen of the carbonyl group (ring) and nitrogen of the azomethine group, and both the nitrate ions are coordinated in a bidentate fashion. The other four ligands (namely, HBAAP, HNAAP, AIPAAP and BIPAAP) function as neutral terdentate ligands bonding also through the oxygen of the phenolic OH (for HBAAP and HNAAP) and the oxygen of the side-chain carbonyl group (for AIPAAP and BIPAAP), in addition to the two sites mentioned above, and both nitrate ions act as monodentate ligands. Hence in the present series of complexes a coordination number of eight may be assigned to the uranyl ion.

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