

TABLE 1 — ANALYTICAL AND MAGNETIC MOMENT DATA OF THE COMPLEXES

Complexes	Analytical data, Found (Calc.)				μ_{eff} at 295°K (BM)
	Metal (%)	N (%)	Anions (%)	Loss of H ₂ O (%)	
MnLCl ₂	22.12 (22.43)	17.25 (17.14)	28.73 (28.93)	—	5.98
MnL ₂ Cl ₂	14.89 (15.09)	23.19 (23.08)	19.84 (19.93)	—	6.05
MnL ₂ Br ₂ ·1.5H ₂ O	11.32 (11.44)	17.33 (17.50)	33.12 (33.27)	5.48 (5.62)	6.01
MnL ₂ I ₂ ·2.5H ₂ O	9.32 (9.42)	14.31 (14.41)	43.38 (43.51)	6.34 (6.17)	5.98
MnL ₂ (NO ₃) ₂ ·2H ₂ O	12.07 (12.13)	24.61 (24.71)	—	8.20 (7.95)	5.98
MnL ₂ (NCS) ₂ ·2H ₂ O	12.21 (12.34)	25.22 (25.15)	—	7.72 (8.09)	5.96
Mn(Bzt) ₂ ·2.5H ₂ O	16.41 (16.33)	24.80 (25.01)	—	13.51 (13.39)	6.02
[Mn(Bzt)(CH ₃ COO)] _n	23.38 (23.58)	18.28 (18.10)	—	—	5.92

L = benzotriazole (BztH).

vibrations in the same region. The strong and broad $\nu(\text{CN})$ band at 2060 cm^{-1} is attributed to ionic thiocyanate group¹³. Acetato complex $[\text{Mn}(\text{Bzt})(\text{CH}_3\text{COO})]_n$ exhibits strong and broad $\nu(\text{COO})$ bands at 1535 and 1470 cm^{-1} . The ionic acetate group shows (COO) bands at 1578 and 1425 cm^{-1} , which are expected to have greater separation in mono-coordinated acetate group. In the case of bidentate acetate group, the separation of (COO) stretching bands should be reduced¹⁴. Low separation of (COO) bands in the present case is probably due to the bridging nature of the acetate group in the complex, $[\text{Mn}(\text{Bzt})\text{CH}_3\text{COO}]_n$. The disappearance of $\nu(\text{N}-\text{H})$ band of ligand at 3210 cm^{-1} suggests the deprotonation of (N-H) and coordination of the ligand as a monobasic acidic group. In the IR spectrum of neutral bis chelate, $\text{Mn}(\text{Bzt})_2 \cdot 2.5\text{H}_2\text{O}$, the disappearance of $\nu(\text{N}-\text{H})$ suggests the deprotonation and coordination of ligand through N-H nitrogen. All the hydrated complexes exhibit a strong and broad band near 3450 cm^{-1} due to $\nu(\text{O}-\text{H})$ of water molecules.

The electronic absorption spectra of the complexes do not exhibit any bands perhaps due to weak intensity of spin-allowed $d-d$ transitions.

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U(IV) Complexes with 8-Hydroxyquinoline, 8-Hydroxy-7-iodoquinoline-5-sulphonic Acid, Quinaldine Acid & Pyridine-2,6-dicarboxylic Acid

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Stable U(IV) chelates with the title ligands have been prepared from U(IV) acetate and characterized by IR, electronic and magnetic susceptibility data which indicate that coordination number of U(IV) in these complexes is more than six.

WENDLANDT and Horton¹ have synthesized and characterized U(IV) complexes of the type, $\text{U}(\text{O}_x)_4\text{HO}_x$ with 8-hydroxyquinoline and 5,7-dibromo- and 5,7-dichloro-8-hydroxyquinolines. On addition of quinaldine acid to an aqueous solution of U(IV) chloride, complexes of the types, $\text{UCl}_4 \cdot 8\text{C}_9\text{H}_7\text{NCOOH}$ and $\text{UCl}_2 \cdot (\text{C}_9\text{H}_7\text{NCOO})_2 \cdot 2\text{C}_9\text{H}_7\text{NCOOH}$, have been isolated depending on pH^2 . Complex formation with picolinic acid and N-oxypicolinic acid in solution has been indicated³.

In the present work stable chelates of U(IV) acetate with 8-hydroxyquinoline, 8-hydroxy-7-iodoquinoline-5-sulphonic acid, quinaldine acid and pyridine-2,6-dicarboxylic acid have been prepared and characterized on the basis of IR, electronic and magnetic susceptibility data.

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U(IV) acetate was prepared by the reduction of uranyl chloride with zinc amalgam and acetic acid⁴. 8-Hydroxyquinoline (BDH), 8-hydroxy-7-iodoquinoline-5-sulphonic acid (Riedel), quinaldonic acid (Fluka AG) and pyridine 2,6-dicarboxylic acid (Fluka) were used as such. Ethanol was purified and dried by usual methods.

Tetrakis(8-quinolinolato)U(IV) (chelate-I) — Quinolin-8-ol (0.86 g) and U(IV) acetate (0.69 g) were mixed in ethanol (40 ml). Immediately greenish-yellow complex separated out which was filtered, washed with ethanol and dried under vacuum (Found: U, 29.07; C, 52.31; H, 3.31; N, 6.63. Reqd U, 29.24; C, 53.07; H, 2.95; N, 6.88%); $\mu_{\text{eff}} = 2.57$ BM.

Bis(7-iodo-5-sulphonic acid-8-quinolinolato)oxouranium(IV) (chelate-II) — U(IV) acetate (0.41 g) and 8-hydroxy-7-iodoquinoline-5-sulphonic acid (1.22 g) were refluxed in water (50 ml) for 1 hr and the reaction mixture allowed to stand overnight when a red coloured complex separated. It was filtered and recrystallized from ethanol and dried *in vacuo* over H_2SO_4 (Found: U, 26.81; C, 23.02; H, 1.15; N, 3.01. Reqd U, 24.95; C, 22.64; H, 1.05; N, 2.93%); $\mu_{\text{eff}} = 1.77$ BM.

(Triacetato)quinaldinatoU(IV) (chelate-III) — Quinaldonic acid (1.22 g) and U(IV) acetate (1.66 g) were refluxed in ethanol (40 ml) for 1 hr when a green-coloured complex separated, which was filtered, washed with ethanol and dried *in vacuo* (Found: U, 40.37; C, 31.61; H, 2.25; N, 2.44. Reqd U, 40.56; C, 32.71; H, 2.56; N, 2.38%); $\mu_{\text{eff}} = 2.0$ BM.

(Triacetato)(pyridine-2,6-dicarboxylato)U(IV) (chelate IV) — Pyridine-2,6-dicarboxylic acid (0.56 g) and U(IV) acetate (0.78 g) were refluxed in ethanol (40 ml) for 4 hr. The greenish complex was filtered, washed with ethanol and dried *in vacuo* (Found: U, 39.69; C, 26.95; H, 2.13. Reqd U, 40.97; C, 26.84; H, 2.23); $\mu_{\text{eff}} = 3.06$ BM.

All these chelates are quite stable at room temperature, are very slowly oxidized by air and do not melt up to 250° but decompose at higher temperatures. On heating they start decomposing and lose weight continuously till they are converted to U_3O_8 at about 600°. Chelates (III) and (IV) are insoluble in most of the organic solvents. However, chelates (I) and (II) are sparingly soluble in ethanol and water giving pale yellow and red solutions respectively.

In chelate (I) the absence of IR bands (positions in cm^{-1}) in the region 1060-850 is an evidence for the absence of O-U-O multiple bonds⁵. The strong bands at 1028, 942, 910 and 857 in chelate (II) indicate the presence of UO^{2+} (ref. 5). Strong bands in the region 600-400 in complexes (I) to (IV) indicate the presence of strong U-N and U-O bonds⁶. The bands at 1620, 1580 and 1535 in quinaldonic acid shift to higher frequencies indicating coordination of the ligand through carboxylic group⁷. In the chelate (III) the bands at 1555 ($\nu_{\text{as}} \text{OCO}$) and 1420, 1280 ($\nu_{\text{s}} \text{OCO}$) indicate the presence of acetate group⁶. The band at 1685 in pyridine-2,6-dicarboxylic acid shifts to 1650 in the complex indicating coordination through carboxylic group. The band at 1560 shifts to 1580 which conforms to coordination from nitro-

gen of the ring. The bands at 1580, 1520 ($\nu_{\text{as}} \text{OCO}$) and 1300, 1218 ($\nu_{\text{s}} \text{OCO}$) in the chelate (IV) may also be due to the presence of the acetate group⁶.

The strong intensity of reflectance spectral bands of chelates (I) to (IV) indicates that the complexes lack a centre of symmetry and electronic transitions are not Laporte-forbidden. The reflectance spectra of these chelates resemble the spectra of U(IV) compounds in which uranium is eight coordinated^{8,9}.

The μ_{eff} values of 2.57 and 3.06 BM for chelates (I) and (IV) are comparable to those reported by other workers⁸⁻¹¹, where U(IV) is probably eight coordinated. Very low magnetic moments of 1.77 and 2.00 B. M. for chelates (II) and (III) respectively may be attributed to strong metal-metal interaction, probably due to magnetic exchange involving oxygen bridging.

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Complexes of Ge(IV) & Sn(IV) Chlorides with N-Salicyloylhydrazine, N-Acetyl-N'-salicyloylhydrazine & N-Benzoyl-N'-salicyloylhydrazine

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Ge(IV) chloride forms 1:2 (metal: ligand) adducts with N-salicyloylhydrazine (SH), N-acetyl-N-salicyloylhydrazine (ASH) and N-benzoyl-N'-salicyloylhydrazine (BSH) while Sn(IV) chloride yields 1:1 adducts with ASH and BSH and 1:1 as well as 1:2 adducts with SH. Infrared spectral studies in the region 4000-200 cm^{-1} have been used to determine the bonding sites in these compounds. Molar conductance in nitrobenzene shows the compounds to be nonelectrolytes.

COMPLEXES of a number of acylhydrazines have been reported with different metal ions¹⁻⁴ and Lewis acids⁵. However, the coordination compounds of N-salicyloylhydrazine (SH), N-acetyl-N-salicyloylhydrazine (ASH) and N-benzoyl-N-sali-