

Aromatic Imine Complexes of Selenium and Tellurium

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Complexes of Selenium(IV) and Tellurium(IV) were synthesized and characterized by elemental analysis, conductivity measurements, and infrared and nuclear magnetic resonance spectroscopic data. The complexes were shown to have 1:2 or 1:4 (metal:chelate) stoichiometry with a coordination number of six. 1:2 stoichiometry was most prevalent. 1:4 stoichiometry occurred when a methyl group was bonded to the azomethine carbon of the imine complex. The imine complexes were bidentate when coordinating with selenium and unidentate when coordinating with tellurium.

Introduction

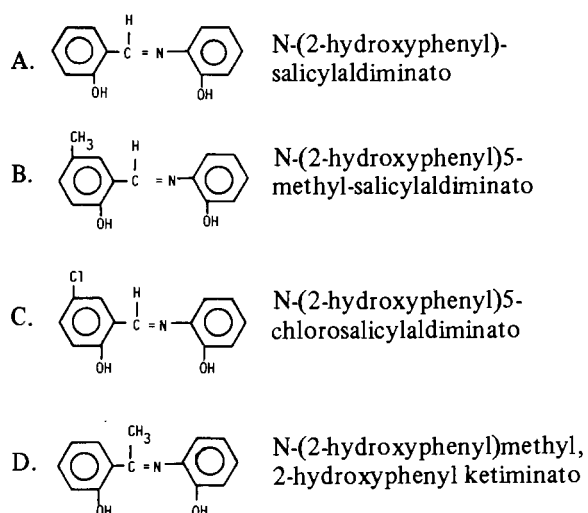
Ligands containing more than two coordinating sites have been extensively investigated [1–3], and among these, ligands with three coordinating nitrogen atoms have been shown to form bidentate chelating ligands in many complexes [4–10]. Only two out of three possible binding sites are actually coordinated to a central metal ion. Tetravalent metal ions form complexes with these chelates wherein a coordination number of six is achieved, and the two chelates occupy four equatorial positions in an octahedron [11–13].

There has been a limited amount of work done on Schiff bases containing one nitrogen and two oxygens potentially available for coordination. In this work a series of selenium and tellurium Schiff base complexes have been synthesized and characterized.

Experimental

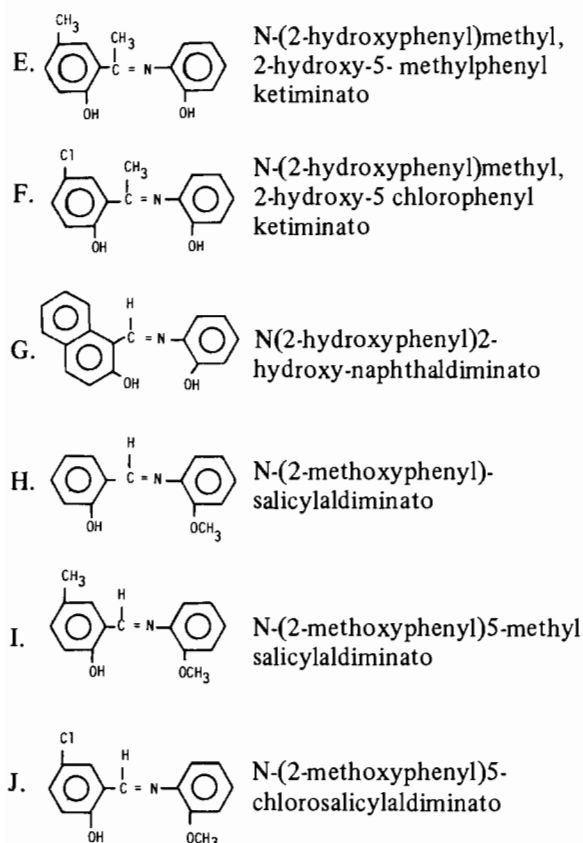
All the chemicals used in this work were of reagent grade. The salicylaldehydes (A–C) were prepared by the reaction of (2-hydroxy)aniline with substituted (2-hydroxy)benzaldehyde. The salicylaldehydes (H–J) were prepared by the reaction of (2-methoxy)aniline with substituted (2-hydroxy)benzaldehyde. The ketimines (D–F) were prepared by the reaction of (2-hydroxy)aniline with substituted methyl, 2-hydroxyphenylketone. The naphthaldehyde (G) was prepared by the reaction of (2-hydroxy)aniline with 2-hydroxy α -naphthalenecarboxaldehyde. All the reagents were mixed in equimolar proportions. The reagents were dissolved in ethanol and the mixture was maintained at constant temperature (25 °C) in a water bath for one hour.

The following imines were prepared:



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The selenium(IV) and tellurium(IV) complexes were prepared by mixing the respective metal tetrachloride with the ligands in dry benzene in the molar ratio of 1:2. Tables I and II correlate each ligand

A–J with its corresponding selenium (I–VIII) or tellurium (IX–XVIII) complex.

The resulting complex was then filtered, washed repeatedly with anhydrous benzene using a Soxhlet extractor, and finally dried under vacuum over P_2O_5 . Due to the toxic nature of these complexes, every precaution was taken in order not to handle them.

Elemental analyses were carried out by a procedure discussed elsewhere [14]. Selenium and tellurium were determined as their respective metals. Chlorine was determined as the silver chloride precipitate, while the method of Kjeldahl was used to determine the nitrogen content of the complexes.

Conductivities were measured in dimethylformamide (DMF) using an Elico-CM-82 conductivity bridge with a cell having a cell constant of 0.829 cm^{-1} . All conductivity measurements were performed at room temperature using 10^{-3} M solutions of complex.

The infrared spectra (IR) from 4000 to 200 cm^{-1} were obtained using a Perkin-Elmer 180 spectrophotometer. Samples were prepared as KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded using a S-60-C PMR instrument. All NMR samples were dissolved in deuterated dimethylsulfoxide (d_6 -DMSO), and tetramethylsilane (TMS) was used as the internal standard.

Results and Discussion

All the complexes are colored, and soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The elemental analyses (see Tables I and II)

TABLE I. Analytical and Physical Data for Selenium(IV) Complexes.^a

Ligand	Complex Number	Empirical formula of the complex	M.P. °C	%Se	%N	%Cl	Molar Conduc. ($\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
A	I	$(C_{13}H_{10}NO_2)_2SeCl_2$	215	13.70 (13.76)	4.78 (4.88)	12.35 (12.37)	65.30
B	II	$(C_{14}H_{12}NO_2)_2SeCl_2$	233	13.11 (13.12)	4.55 (4.65)	11.89 (11.79)	83.80
C	III	$(C_{13}H_9NO_2Cl)_2SeCl_2$	217	12.20 (12.28)	4.31 (4.35)	11.11 (11.04)	76.70
E	IV	$(C_{60}H_{58}N_4O_8)_2SeCl_2$	>290	7.19 (7.10)	5.01 (5.04)	6.29 (6.39)	45.60
F	V	$(C_{56}H_{46}N_4O_8Cl_4)_2SeCl_2$	>300	6.50 (6.61)	4.71 (4.69)	5.85 (5.95)	46.00
H	VI	$(C_{14}H_{12}NO_2)_2SeCl_2$	160	13.13 (13.12)	4.70 (4.65)	11.80 (11.79)	60.00
I	VII	$(C_{15}H_{14}NO_2)_2SeCl_2$	165	12.83 (12.53)	4.53 (4.44)	11.42 (11.27)	64.60
J	VIII	$(C_{14}H_{11}NO_2Cl)_2SeCl_2$	164	11.67 (11.77)	4.27 (4.17)	10.49 (10.48)	63.00

^aFigures in the parentheses are calculated values.

TABLE II. Analytical and Physical Data for Tellurium(IV) Complexes.^a

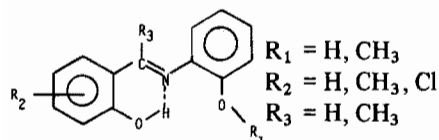
Ligand	Complex Number	Empirical formula of the complex	M.P. °C	%Se	%N	%Cl	Molar Conduc. (ohm ⁻¹ cm ² mol ⁻¹)
A	IX	(C ₁₃ H ₁₁ NO ₂) ₂ TeCl ₄	220	18.45 (18.35)	4.04 (4.03)	20.43 (20.42)	136.70
B	X	(C ₁₄ H ₁₃ NO ₂) ₂ TeCl ₄	>290	17.62 (17.64)	3.89 (3.87)	19.73 (19.63)	94.30
C	XI	(C ₁₃ H ₁₀ NO ₂ Cl) ₂ TeCl ₄	230	16.68 (16.69)	3.67 (3.66)	18.63 (18.58)	146.24
D	XII	(C ₁₄ H ₁₃ NO ₂) ₂ TeCl ₄	160	17.72 (17.64)	3.80 (3.87)	19.53 (19.63)	122.40
E	XIII	(C ₁₅ H ₁₅ NO ₂) ₂ TeCl ₄	195	16.99 (16.98)	3.75 (3.73)	18.97 (18.90)	133.80
F	XIV	(C ₁₄ H ₁₂ NO ₂ Cl) ₂ TeCl ₄	>300	16.23 (16.10)	3.54 (3.53)	17.93 (17.92)	134.10
G	XV	(C ₁₇ H ₁₃ NO ₂) ₂ TeCl ₄	225	16.00 (16.04)	3.50 (3.52)	17.78 (17.85)	117.80
H	XVI	(C ₁₄ H ₁₃ NO ₂) ₂ TeCl ₄	190	17.65 (17.64)	3.83 (3.87)	19.70 (19.63)	133.00
I	XVII	(C ₁₅ H ₁₅ NO ₂) ₂ TeCl ₄	183	16.99 (16.98)	3.75 (3.73)	18.93 (18.90)	121.40
J	XVIII	(C ₁₄ H ₁₂ NO ₂ Cl) ₂ TeCl ₄	180	16.00 (16.10)	3.52 (3.53)	17.93 (17.92)	123.30

^aFigures in the parentheses are calculated values.

agree well with 1:2 or 1:4 (metal:chelate) stoichiometry. For selenium complexes, the molar conductivities are in the range of 45–84 ohm⁻¹ cm² mol⁻¹. These values approach those expected for 1:1 electrolyte in DMF. Tellurium(IV) complexes on the other hand, behave as 1:2 electrolytes in DMF as indicated by the molar conductivities which fall in the range of 94–147 ohm⁻¹ cm² mol⁻¹.

Infrared Spectra

In Schiff bases derived from 2-hydroxy aniline (A–G), and 2-methoxy aniline (H–J) a broad weak band is observed in the range, 2680–2740 cm⁻¹. Baker and Schulgin attribute the band to intramolecular hydrogen bonding [15]. The Schiff base chelates can be formulated to have the following structure:



In selenium complexes, this band is absent, thereby suggesting that the hydroxy group of the Schiff base has been utilized in bond formation. In tellurium complexes the band at 2700 cm⁻¹ is present and the intramolecular-bonded hydroxy group is not involved in chelation.

In accordance with previously published data [16–18], the sharp, strong band in the region,

1620–1635 cm⁻¹, in the spectra of Schiff bases is assigned to $\nu(\text{C}=\text{N})$. However, in the majority of the complexes, the band appears in the region 1645–1660 cm⁻¹, and the high frequency shift observed in the complexes suggests that the coordination has taken place through the azomethine nitrogen to the metal moiety. Similar observations have been made by several researchers [10, 19, 20]. Complexes IV, XII, and XIII exhibit a band at 1500 cm⁻¹; these selenium and tellurium complexes have a methyl group bonded to the carbon of the azomethine moiety, and the methyl group may be affecting the $\nu(\text{C}=\text{N})$ stretch. Metal–nitrogen bonding is substantiated by the presence of bands in the range 530–580 cm⁻¹ which are assigned to Se–N or Te–N depending upon the complex. These assignments correlate with those made previously by Biradar and co-workers [21–23].

A medium intensity band that appears in the region 1280–1290 cm⁻¹ is ascribed to the phenolic C–O stretch [24]. In selenium complexes the $\nu(\text{C}=\text{O})$ band can be observed at 1300–1310 cm⁻¹. The shift to higher frequency indicates that the 2-hydroxy group has taken part in the coordination. The phenolic C–O stretch does not shift in the tellurium complexes.

NMR Spectra

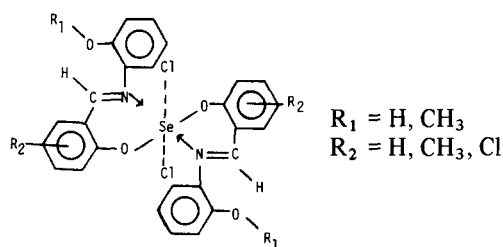
The NMR spectra of the Schiff bases (A and B) and the selenium and tellurium complexes II and IX were evaluated. The spectrum of N-(2-hydroxy-

phenyl) 5-methylsalicylaldehyde (B) is characterized by five signals at 12.95, 9.80, 9.07, 6.80 to 7.80 and 2.40 ppm (relative to TMS), and these are attributed to the hydroxy proton of the salicylidene moiety, the hydroxy proton of the anilinic moiety, the methine proton of the azomethine moiety, the phenyl protons and the methyl group respectively. On complexation to form complex II, the signal at 12.95 ppm disappears indicating that the 2-hydroxy group of the salicylidene moiety, has taken part in the coordination to selenium.

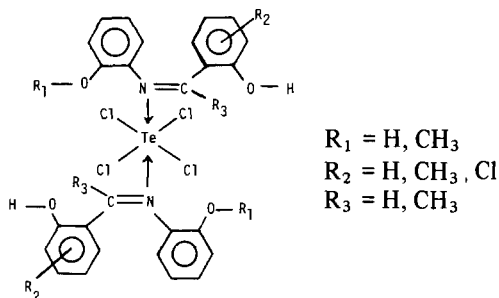
The spectrum of N-(2-hydroxyphenyl) salicylaldehyde (A) is characterized by four signals at 12.90, 9.75, 9.07 and 6.80–7.80 ppm with assignments analogous to those for Schiff base (B). On complexation to form complex (IX) the signal at 12.90 ppm does not shift, indicating a lack of coordination between the hydroxy oxygen and tellurium. This substantiates the results obtained from IR spectroscopy.

Conclusions

Complexes of selenium and tellurium with Schiff base chelates were synthesized and characterized. The elemental analyses and conductivity data prove the existence of 1:2 and 1:4 (metal:chelate) stoichiometry in the complexes. The IR data and NMR results indicate that the hydroxy group of the aldehydic moiety coordinates to selenium, but not with tellurium. Tellurium is a 'softer' acid than selenium and the electron-donating oxygen may not have a propensity for associating with tellurium. This lack of bonding between oxygen and tellurium results in monodentate chelation between the imine and tellurium; whereas in the selenium complexes, the majority of the imines (I–III, VI–VIII) are bidentate. In complexes, IV and V, the elemental analyses confirm a 1:4 (metal:chelate) stoichiometry. These complexes have a methyl group coordinated to the azomethine nitrogen, and this might hinder the coordination of the azomethine nitrogen to the selenium. The complexes appear to be octahedral with two chlorines and four monodentate ligands occupying the corners of the octahedron. Complex VI, although containing a methyl group coordinated to the azomethine nitrogen has a 1:2 (metal:chelate) stoichiometry. The IR and NMR data confirm that the azomethine nitrogen may be involved in the coordination to selenium and tellurium, but that the hydroxy group of the aniline moiety does not appear to be coordinated in any of the selenium or tellurium complexes. Based on the results and in agreement with the results obtained for analogous (*p*-sulfonamido) Schiff base chelates of selenium and tellurium [25], the following tentative structures are proposed (excluding complexes IV–VI):



Tentative Structure for Complexes I–III, VII–VIII



Tentative Structure for Complexes IX–XVIII

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