Inorganica Chimica Acta, 76 (1983) L131–L134

Complexes of Tellurium with Vanillydene-Schiff Bases

T. M. AMINABHAVI*, W. E. RUDZINSKI**

Department of Chemistry, Southwest Texas State University, San Marcos, Tex. 78666 U.S.A.

N. S. BIRADAR and C. S. PATIL

Department of Chemistry, Karnatak University, Dharwas, India 580003

Received September 3, 1982

Introduction

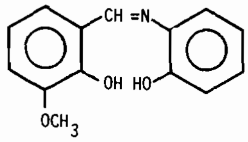
In recent years there has been a considerable amount of interest in the complexes of transition metals with a variety of aromatic-Schiff base chelates [1–5]. As a part of our broad-based research dealing with the complexation chemistry of selenium(IV) and tellurium(IV) [6–9], a number of vanillydene-Schiff base complexes have been synthesized and subsequently characterized using infrared (IR) and nuclear magnetic resonance (NMR) spectral data, as well as by conductance measurements.

Experimental

All the chemicals used in this work were of reagent grade. The ligands were prepared by reacting *o*-vanillal with substituted aniline (compounds A–F), 4-amino-diphenylhydrazine (compound G), 4-amino-diphenylamine (compound H), ethylenediamine (compound I) or propylene diamine (compound J). The reagents were dissolved in ethanol and the mixture was maintained at constant temperature (25 °C) in a water bath for one hour.

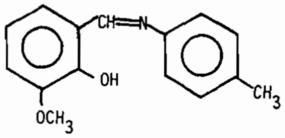
The following compounds were prepared:

A



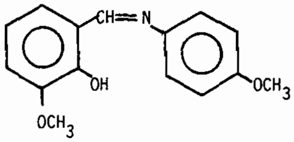
N-(2-hydroxyphenyl)*o*-vanillaldimine

B



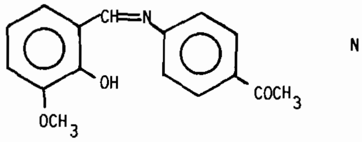
N-(4-methylphenyl)*o*-vanillaldimine

C



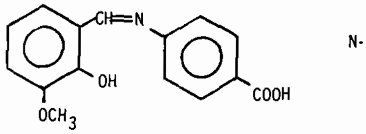
N-(4-methoxyphenyl)*o*-vanillaldimine

D



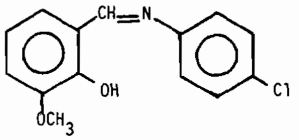
N-(4-acetophenyl)o-vanillaldimine

E



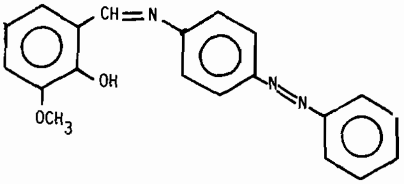
N-(4-carboxyphenyl)*o*-vanillaldimine

F



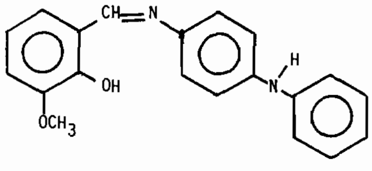
N-(4-chlorophenyl)*o*-vanillaldimine

G



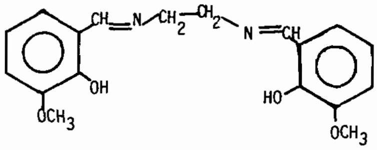
N-(ν-diphenylhydrazine)*o*-vanillaldimine

H



N-(ν-diphenylamine)*o*-vanillaldimine

I



di(*o*-vanillal)ethylemediimine

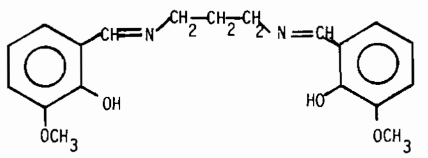
---

*On leave from Karnatak University, Dharwad, India 580003.

**Author to whom correspondence should be addressed.

0020-1693/83/0000-0000/$03.00

J



di(*o*-vanillal)propylenediimine

The tellurium(IV) complexes were prepared by mixing tellurium tetrachloride with the ligands in dry benzene in the molar ratio of 1:2. The resulting mixture was then allowed to react for several hours at room temperature. The complex was then filtered, washed repeatedly with anhydrous benzene using a Soxhlet extractor, and finally dried under vacuum over P_2O_5. Table I correlates each ligand (A–H) with its corresponding complex (I–X).

Elemental analyses were carried out by a procedure discussed elsewhere [10]. Tellurium was determined as tellurium metal. Chlorine was determined as the silver chloride precipitate, while sulfur was determined as the barium sulfate salt. 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

Analytical Data

All the complexes are colored and insoluble in common organic solvents, but soluble in DMF and DMSO. The elemental analyses agree well with 1:1 stoichiometry (metal:ligand). The molar conductivities are in the ragne 100–136 ohm^{-1} cm^2 mol^{-1}. These values approach those expected for 1:2 electrolyte in DMF [11].

Infrared Spectra

Important IR frequencies and their assignments are tabulated and available upon request from the author to whom all correspondence should be addressed.

A broad weak band observed in the ligands in the range, 2700–2600 cm^{-1}, is assigned to an intramolecular hydrogen bond [12, 13]. The band does not disappear on complexation with tellurium

TABLE I. Analytical and Physical Data for the Tellurium(IV) Complexes of Vanillydene-Schiff Bases.[a]

Ligand	Complex No.	Empirical Formula of the Complex	M.P. °C	% Te	% N	% Cl	Molar Conductance ohm^{-1} cm^2 mol^{-1}
A	I	$(C_{14}H_{13}NO_3)TeCl_4$	185	25.01 (24.90)	2.70 (2.73)	27.70 (27.71)	101.20
B	II	$(C_{15}H_{15}NO_2)TeCl_4$	151	25.09 (25.00)	2.76 (2.74)	27.87 (27.82)	115.70
C	III	$(C_{15}H_{15}NO_3)TeCl_4$	152	24.25 (24.24)	2.95 (2.66)	26.84 (26.97)	114.30
D	IV	$(C_{16}H_{15}NO_3)TeCl_4$	166	23.71 (23.70)	2.84 (2.60)	26.27 (26.37)	102.70
E	V	$(C_{15}H_{13}NO_4)TeCl_4$	185	23.56 (23.61)	2.55 (2.59)	26.26 (26.27)	118.40
F	VI	$(C_{14}H_{12}NO_2Cl)TeCl_4$	181	24.04 (24.03)	2.65 (2.64)	26.67 (26.75)	108.10
G	VII	$(C_{20}H_{17}N_3O_2)TeCl_4$	178	21.26 (21.25)	6.92 (6.99)	23.69 (23.65)	102.90
H	VIII	$(C_{20}H_{18}N_2O_2)TeCl_4$	163	21.75 (21.72)	4.80 (4.77)	24.24 (24.17)	108.70
I	IX	$(C_{18}H_{20}N_2O_4)TeCl_4$	177	21.29 (21.36)	4.60 (4.69)	23.81 (23.77)	136.20
J	X	$(C_{19}H_{22}N_2O_4)TeCl_4$	070	20.80 (20.87)	4.65 (4.58)	23.30 (23.22)	125.60

[a] Figures in the parentheses are calculated values.

TABLE II. NMR Chemical Shifts of Vanillydene-Schiff Bases and Their Tellurium(IV) Complexes.

G	VII	H	VIII	I	IX	Assignments
13.15*	–	13.33	–	13.27	10.23	Hydroxy proton
08.36	09.00	08.50	08.88	08.52	08.70	Methine proton
07.00 to	06.60 to	06.78 to	06.50 to	06.45 to	06.73 to	Phenyl protons
08.00	08.27	07.88	08.10	07.28	07.40	
03.89	03.82	03.89	03.87	03.82	03.88	$-OCH_3$ protons
–	–	–	–	03.93	03.15	ethylene protons
–	–	05.01	–	–	–	NH proton

*In ppm δ.

indicating that the *o*-hydroxy group of the vanillal moiety is not involved in the bonding. An intense band in the range, 1620–1600 cm^{-1} in the ligands, is assigned to ν(C=N) [14–16]; the frequency shifts to the range 1650–1630 cm^{-1} for the tellurium complexes. The observed shift indicates that the azomethine nitrogen is coordinated to the tellurium [17]. A strong band observed around 1660 cm^{-1} in the ligand D and in the complex IV is assigned to ν(C=O). A band at 1580 cm^{-1} in ligand G and in complex VII is assigned to ν(N=N). A band at 3400 cm^{-1} in ligand H and in complex VIII is assigned to ν(N–H). The preceding three bands do not shift on complexation, and so none of the associated atoms are involved in complexation.

The band around 1270 cm^{-1} due to the ν(C–O) in the vanillal moiety of the ligands remains unaffected upon complex formation further substantiating the non-participation of the hydroxy group. The band assignment agrees well with that made by Kovacic [17].

A strong band around 320 cm^{-1} is attributed to ν(Te–Cl) [18, 19].

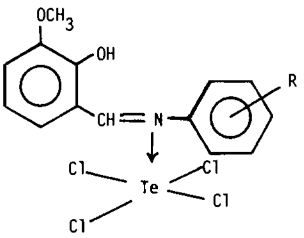
Nuclear Magnetic Resonance Spectra

The NMR chemical shifts for the protons in representative ligands and their tellurium complexes are given in Table II. The ligand spectra are characterized by signals around 13.2 ppm, 8.4 ppm, 6.5–8.3 ppm and 3.9 ppm which can be attributed to hydroxy, methine, phenyl and m-OCH_3 protons respectively. In the ligands H and I, additional peaks observed around 5.6 ppm and 3.9 ppm are ascribed to N–H and ethylene protons respectively. The coordination of the azomethine nitrogen to tellurium in the complexes is clearly demonstrated by a downfield shift of the peak due to the methine proton in the ligands upon complexation.

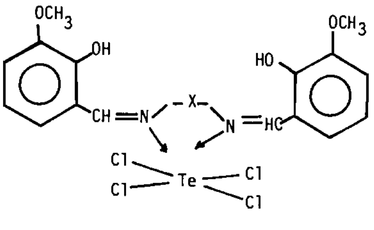
Conclusions

The elemental analyses show that all the complexes have 1:1 (metal:ligand) stoichiometry. The conductance data indicate that the complexes behave as 1:2 electrolytes in DMF. The IR and NMR data reveal that the azomethine nitrogen is involved in the coordination, whereas the *o*-hydroxy group of the vanillal moiety is not coordinating. The tellurium complexes I–VIII are formulated to be pentacoordinated whereas complexes IX and X may be hexacoordinate. The following tentative structures are proposed for the complexes:

Complexes I–VIII



Complexes IX–X



X – $(CH_2)_2$, $(CH_2)_3$

Acknowledgements

T. M. Aminabhavi is extremely grateful to Professor Patrick E. Cassidy of Southwest Texas State University, San Marcos, Texas for his encouragement in the author's research and for hosting him as a post-doctoral fellow in his group. W. E. Rudzinski would like to thank the Robert A. Welch Foundation (Grant AI-809) for support in this work.

References

1 N. S. Biradar and V. H. Kulkami, *J. Less Common Metals, 26,* 355 (1972).

2 N. S. Biradar and V. B. Mahale, *Z. Anorg. Allg. Chem., 388,* 277 (1972).

3 N. S. Biradar, V. B. Mahale and V. H. Kulkarni, *Inorg. Chim. Acta, 7,* 267 (1973).

4 N. S. Biradar and M. A. Pujar, *J. Inorg. Nucl. Chem., 37,* 1291 (1975).

5 K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta, 12,* 109 (1975).

6 W. E. Rudzinski, T. M. Aminabhavi, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta,* in press.

7 W. E. Rudzinski, T. M. Aminabhavi, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta,* in press.

8 T. M. Aminabhavi, W. E. Rudzinski, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta* (submitted for publication).

9 N. S. Biradar, T. M. Aminabhavi, C. S. Patil and W. E. Rudzinski, *Inorg. Chim. Acta* (submitted for publication).

10 A. I. Vogel, 'Textbook of Quantitative Inorganic Analysis', 3rd ed., Longmans, Green and Co., New York, N.Y. (1969).

11 D. A. Couch, P. S. Elmes, J. E. Fergusson, M. L. Greenfield and C. J. Wilkins, *J. Chem. Soc. (A),* 1813 (1967).

12 H. H. Freedman, *J. Am. Chem. Soc., 83,* 2900 (1961).

13 A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc., 81,* 1523 (1959).

14 C. S. Marvel, A. S. Aspey and E. A. Dudley, *J. Am. Chem. Soc., 78,* 4905 (1956).

15 K. Ueno and A. E. Martell, *J. Phys. Chem., 59,* 998 (1955).

16 L. E. Clougherty, J. A. Sousa and G. M. Wyman, *J. Org. Chem., 22,* 462 (1957).

17 J. E. Kovacic, *Spectrochim. Acta, 23A,* 183 (1967).

18 W. R. McWhinnie and P. Thavornyutikarn, *J. Chem. Soc., Dalton,* 561 (1972).

19 E. R. Clark, A. J. Collett and D. G. Naik, *J. Chem. Soc., Dalton,* 1961 (1973).