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Complexes of Hydrazones with Tellurium

T. M. AMINABHAVI, N. S. BIRADAR, C. S. PATIL

Department of Chemistry, Karnatak University, Dharwad, India 580003

and W. E. RUDZINSKI*

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

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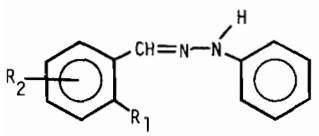
Several complexes of hydrazones with tellurium were prepared and characterized using conductivity measurements and infrared and nuclear magnetic resonance spectra. Elemental analyses confirmed a 1:2 (metal:ligand) stoichiometry. Most of the complexes have proven to be biologically active as evidenced by anti-inflammatory tests.

Introduction

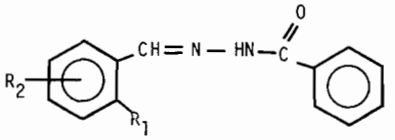
Recently, there has been a considerable amount of interest in the chemistry of hydrazones because of potential pharmacological applications [1–4]. Several metal complexes of hydrazones have been reported [5–6], and as a further contribution to the metal complexation chemistry of selenium(IV) and tellurium(IV) [7–9], a series of hydrazone complexes have been synthesized, characterized and their biological activity determined. The complexes have been characterized using infrared and nuclear magnetic resonance spectral data as well as by conductance measurements. The biological activity has been evaluated using anti-inflammatory activity tests.

Experimental

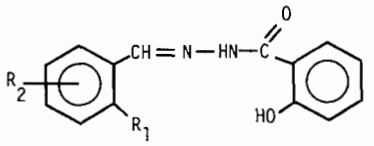
All chemicals used in this work were of reagent grade. The ligands were prepared according to methods published previously [10, 11]. The following ligands were prepared:



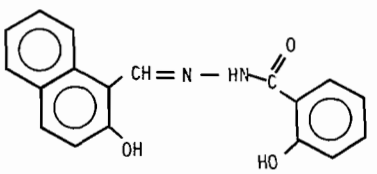
Ligand	R_1	R_2	*Name*
A	H	H	Benzalphenylhydrazone
B	OH	H	2-hydroxybenzalphenylhydrazone
C	OH	3-OCH_3	2-hydroxy-3-methoxy-benzalphenylhydrazone



Ligand	R_1	R_2	*Name*
D	H	H	Benzalbenzoylhydrazone
E	OH	H	2-hydroxybenzalbenzoyl-hydrazone
F	OH	5-Me	2-hydroxy-5-methylbenzal-benzoylhydrazone
G	OH	5-Cl	2-hydroxy-5-chlorobenzal-benzoylhydrazone
H	OH	3-OCH_3	2-hydroxy-3-methoxybenzal-benzoylhydrazone



Ligand	R_1	R_2	*Name*
I	H	H	Benzalsalicylhydrazone
J	OH	H	2-hydroxy-benzalsalicyl-hydrazone
K	OH	5-Me	2-hydroxy-5-methylbenzalsalicyl-hydrazone
L	OH	5-Cl	2-hydroxy-5-chlorobenzalsalicyl-hydrazone



Ligand	*Name*
M	2-hydroxy-2-naphthalsalicylhydrazone

*Author to whom all correspondence should be addressed.

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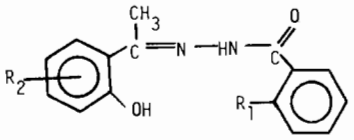
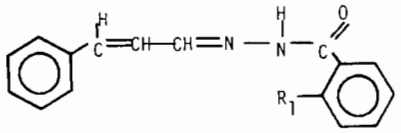
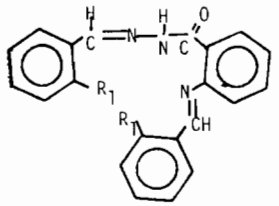


Ligand	R_1	R_2	*Name*
N	H	5-Me	Methyl-(2-hydroxy-5-methyl-phenyl)ketiminobenzoylhydrazone
O	H	5-Cl	Methyl-(2-hydroxy-5-chlorophenyl) ketiminobenzoylhydrazone
P	OH	5-Me	Methyl-(2-hydroxy-5-methyl-phenyl)ketiminosalicylhydrazone



Ligand	R_1	R_2	*Name*
Q	H	–	3-phenylpropenalbenzoylhydrazone
R	OH	–	3-phenylpropenalsalicylhydrazone



Ligand	R_1	R_2	*Name*
S	H	–	Benzal(2-phenylimine)benzoyl-hydrazone
T	OH	–	2-hydroxybenzal[2-(2-hydroxy-phenyl)imine] benzoylhydrazone

The tellurium(IV) complexes were prepared by mixing the respective metal tetrachloride with the ligand in dry benzene in the molar ratio 1:2. The resulting 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–T) with its corresponding tellurium (I–XX) complex.

Elemental analyses were carried out by a procedure discussed elsewhere [12]. Tellurium was determined as the 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.

The anti-inflammatory activity test was carried out by using the carrageenan-induced rat paw edema assay of Winter *et al.* [13]. 100 mg/kg body weight was found to be a safe dose level in acute toxicity studies. Phenylbutazone known to have substantial anti-inflammatory activity was used as a reference compound. 4% gumacacia was used as a control.

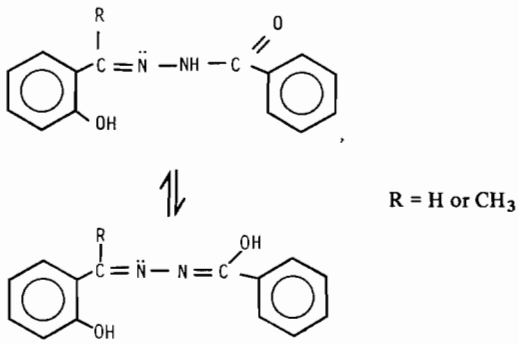
Results and Discussion

Analytical Data

The results of the elemental analyses are given in Table I. The data indicate that all the complexes (except for XIX and XX) have 1:2 (metal:ligand) stoichiometry. Complexes XIX and XX have 1:1 (metal:ligand) stoichiometry. The complexes are colored and amorphous in nature, and insoluble in most organic solvents. The complexes are soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The conductance values in dimethylformamide are in the range 100–173 ohm^{-1} cm^2 mol^{-1}, which indicates that the complexes behave as 1:2 electrolytes.

Infrared Spectra

It is known that benzoyl hydrazones (ligands D–T) exhibit keto-enol tautomerism and as such they can exist in one of the following two forms [14, 15]:



If the ligands are in the keto form, the ν(N–H) and ν(C=O) absorption bands will appear in the IR spectra; whereas the absence of these two absorptions may be indicative of the enol form. All the ligands show a consistent medium intensity band in the range 3380–3190 cm^{-1}; this is attributed to ν(N–H). A broad weak band for some of the ligands in the range 2850–2700 cm^{-1}, is assigned to an intramolecular

TABLE I. Analytical and Physical Data for Hydrazone Complexes of Tellurium(IV).

Ligand	Complex	Empirical formula of the complex	M.P. °C	%Te	%N	%Cl	Molar Cond. (ohm^{-1} cm^2 mol^{-1})
A	I	$(C_{13}H_{12}N_2)_2TeCl_4$	60.0	19.22 (19.29)*	8.42 (8.47)	21.39 (21.47)	151.00
B	II	$(C_{13}H_{12}N_2O)_2TeCl_4$	85.0	18.30 (18.40)	8.00 (8.08)	20.50 (20.48)	152.44
C	III	$(C_{14}H_{14}N_2O_2)_2TeCl_4$	80.0	17.00 (16.94)	7.23 (7.43)	18.88 (18.85)	145.38
D	IV	$(C_{14}H_{12}N_2O)_2TeCl_4$	97.0	18.00 (17.79)	7.80 (7.81)	19.81 (19.79)	129.36
E	V	$(C_{14}H_{12}N_2O_2)_2TeCl_4$	115.0	17.00 (17.03)	7.50 (7.47)	18.92 (18.95)	101.10
F	VI	$(C_{15}H_{14}N_2O_2)_2TeCl_4$	108.0	16.48 (16.41)	7.22 (7.20)	18.20 (18.27)	111.17
G	VII	$(C_{14}H_{11}N_2O_2Cl)_2TeCl_4$	115.0	15.62 (15.59)	6.94 (6.84)	17.42 (17.35)	112.63
H	VIII	$(C_{15}H_{14}N_2O_3)_2TeCl_4$	80–110	15.81 (15.76)	7.00 (6.92)	17.59 (17.54)	129.60
I	IX	$(C_{14}H_{11}N_2O_2)_2TeCl_2$	240.0	18.79 (18.86)	8.20 (8.28)	10.44 (10.50)	127.73
J	X	$(C_{14}H_{11}N_2O_3)_2TeCl_2$	225.0	17.93 (17.96)	7.90 (7.88)	10.02 (9.99)	129.73
K	XI	$(C_{15}H_{13}N_2O_3)_2TeCl_2$	240–253	17.22 (17.33)	7.63 (7.60)	9.60 (9.64)	135.67
L	XII	$(C_{14}H_{10}N_2O_3Cl)_2TeCl_2$	280	16.50 (16.41)	7.29 (7.20)	9.09 (9.13)	131.35
M	XIII	$(C_{18}H_{16}N_2O_3)_2TeCl_2$	184	15.72 (15.67)	6.82 (6.88)	8.63 (8.72)	173.12
N	XIV	$(C_{16}H_{16}N_2O_2)_2TeCl_4$	100–110	15.90 (15.84)	7.05 (6.95)	17.64 (17.63)	150.00
O	XV	$(C_{15}H_{13}N_2O_2Cl)_2TeCl_4$	87	15.02 (15.07)	6.59 (6.62)	16.70 (16.78)	119.64
P	XVI	$(C_{16}H_{15}N_2O_3)_2TeCl_2$	100	16.60 (16.69)	7.32 (7.33)	9.33 (9.29)	144.18
Q	XVII	$(C_{16}H_{14}N_2O)_2TeCl_4$	157	16.60 (16.58)	7.22 (7.28)	18.55 (18.45)	135.55
R	XVIII	$(C_{16}H_{13}N_2O_2)_2TeCl_2$	180	17.56 (17.52)	7.70 (7.69)	9.65 (9.75)	143.51
S	XIX	$(C_{21}H_{17}N_3O)TeCl_4$	125	21.34 (21.39)	7.10 (7.04)	23.90 (23.81)	99.61
T	XX	$(C_{21}H_{17}N_3O_3)TeCl_4$	150	20.32 (20.40)	6.80 (6.72)	22.77 (22.70)	115.22

*Figures in parentheses are calculated values.

hydrogen bond [16]. An intense band in the range 1675–1645 cm^{-1} is assigned to ν(C=N) [17, 18]. The presence of these bands confirm that the benzoyl hydrazones exist in the keto form. In ligands A–C (phenylhydrazones) the bands observed in the region 1610–1470 cm^{-1} are assigned to ν(C=N), ν(C=C) and N–H bending vibrations.

In all the complexes (I–XX), the band corresponding to (N–H) is retained. The ν(C=N) band shows a high frequency shift in the complexes I–III, indicating that the nitrogen of the azomethine moiety has coordinated to the tellurium ion. In complexes IV–XVIII, the ν(C=O) and ν(C=N) bands show a low frequency shift, suggesting that either the carbonyl

TABLE II. Proton Magnetic Resonance Chemical Shifts of Hydrazones and Their Tellurium(IV) Complexes.

A	I	J	X	T	XX	Assignments
3.33*	6.63	–	–	3.30	–	NH proton
6.47 to 7.90	6.67 to 8.00	6.47 to 8.10	6.60 to 8.10	6.30 to 8.57	6.30 to 7.97	Phenyl protons
9.80	9.93	8.60	8.63	8.30	8.33	Azomethine proton
–	–	11.33	12.00	11.37	–	Hydroxy proton

*In ppm (δ).

TABLE III. Anti-inflammatory Activity of Hydrazone Complexes of Tellurium(IV).

Complex/Compound	Dose level in mg	Initial reading	Reading after 3 hr	Edema formed	% Inhibition
X	12.50	5.70	7.83	2.13	46.35
XX	17.50	4.80	7.13	2.33	41.30
Phenylbutazone (reference)	16.30	5.40	5.92	0.52	86.90
4% Gumacacia (control)	16.20	6.20	10.17	3.97	–

oxygen, the azomethine nitrogen, or both are coordinatively associated with the tellurium ion. The salicylic C–O stretching vibration shifts from 1275–1295 to 1305–1310 cm^{-1} in complexes IX–XIII and XVIII. This indicates that the hydroxy group of salicylhydrazones is involved in the coordination. The results are corroborated by the fact that complexes IX–XIII, XVI and XVIII, all are coordinated to two chlorides rather than four. The analytical data (see Table I) suggest that the chelating ligands are bidentate with the ortho hydroxy group participating in the bonding. In complexes XIX and XX no shift is observed in the ν(C=O) frequency; hence ν(C=O) does not participate in the bonding.

The complexes all exhibit an intense band around 325 cm^{-1} which has been assigned to ν(Te–Cl) [19, 20]. The strong bands observed around 540 cm^{-1} have been assigned to ν(Te–N) [21–23]. This would seem to indicate that the azomethine nitrogen is coordinated to the tellurium.

Nuclear Magnetic Resonance Spectra

In the PMR spectra, the absorption signals due to N–H, phenyl, methine and hydroxy protons of hydrazones and their tellurium complexes are listed in Table II. The NH proton signal shifts considerably or disappears on complex formation. This may be indicative of a shift from the keto to the enol form, on complexation for ligand T, and a tautomeric shift of the hydrogen from the nitrogen to the doubly-bonded carbon in the phenyl hydrazone, ligand A. The N–H proton signal is not observed in the NMR spectra of ligand J nor in complex X. Since the NMR signal for protons bonded to nitrogen can shift because of hydrogen bonding and because protons bonded to nitrogen experience quadrupole effects, it is very difficult to evaluate the absorption signals. In all the hydrazones and their complexes, the signals observed in the range, 6.3–8.6 are due to phenyl protons. The azomethine proton of the ligands is observed between 8.3 and 10.0, and shifts slightly downfield on complexation. The hydroxy proton is found around 11.35 ± 0.02 and shifts or disappears on complexation.

Anti-inflammatory Activity

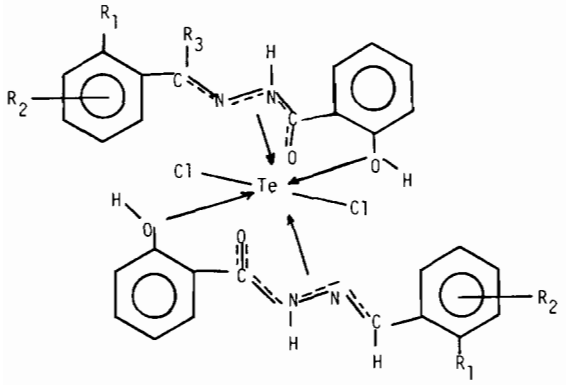
The anti-inflammatory activities of hydrazone complexes of tellurium(IV), in addition to the activity of phenylbutazone are listed in Table III. Hydrazone complexes of tellurium(IV) show mild anti-inflammatory activity as measured by the inhibition of edema when compared with phenylbutazone.

Conclusions

The analytical data suggest that the hydrazone complexes have 1:2 (metal:ligand) stoichiometry, except for the complexes XIX and XX which demonstrate 1:1 (metal:ligand) stoichiometry. The conductance measurements in DMF indicate a 1:2 electrolyte. It has been found that the phenylhydrazones coordinate to the tellurium through the nitrogen of the azomethine group (complexes I–III). The acylhydrazones (ligands D–H, N, O, Q) are monodentate ligands coordinating to tellurium through the

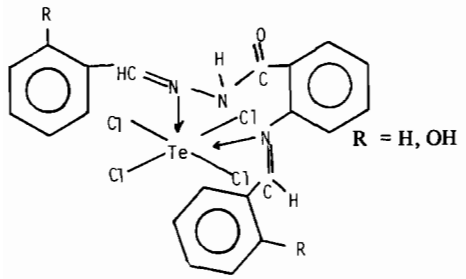
azomethine nitrogen. The acylhydrazones (ligands I–M, P and R) are bidentate chelating ligands coordinating through an azomethine nitrogen and the hydroxy oxygen ortho to the carbonyl group of the salicylhydrazone moiety. Complexes XIX and XX are 1:1 (metal:chelate) complexes where the chelating ligand is bidentate probably bonding to the tellurium through the azomethine nitrogens. The following tentative structures are proposed for the bidentate chelating ligands coordinated to tellurium:

Complexes IX–XII, XVI,



R_1 = H, OH
R_2 = H, 5-CH_3, 5-Cl
R_3 = H, -CH_3

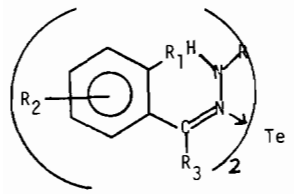
Complexes XIX, XX



R = H, OH

The following are tentative structures for the monodentate chelating ligands coordinated to tellurium:

Complexes I–VIII, XIV, XV



R_1 = H, OH
R_2 = H, 3-OCH_3, 5-Me, 5-Cl
R_3 = H, -CH_3

All complexes are formulated to be octahedral.

Acknowledgements

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