STUDY OF CHARGE – TRANSFER BETWEEN SOME NEW ORGANOTELLURIUM COMPOUNDS AND THEIR APPLICATION IN BIOLOGICAL ACTIVITY

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Abstract

A new telluride's (2-Imino-3-Tellurapiperidine and their Halo-derivatives) are used as a donor to form 1:2 donor – accepter complexes with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The $n \longrightarrow \pi^*$ charge transfer (CT) complexes have been investigated spectrophotometrically in dimethyl sulfoxide (DMSO) solution.

The good yield obtained derivatives were purified and characterized using elemental analysis, UV-vis, IR, ^{1}H NMR spectra and solid conductivity measurements . The solid 1:2 complexes show evidences of semi conducting properties. The new telluride's show antibacterial activity.

Keywords :Heterocyclic tellurium, 2, 3-dichloro-5, 6- dicyanobenzoquinone (DDQ), Charge Transfer, Solid conductivity, and antibacterial activity.

Introduction

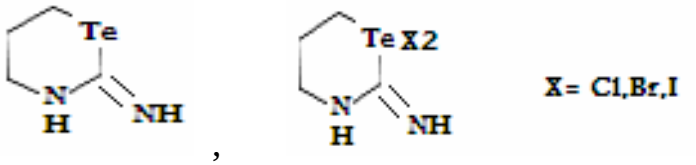
Recent developments in chemical research have shown that there is a considerable interest in the chemistry of Organic Selenocyanates and Tellurocyanates. Works in this field are widely published [1-4]. Spencer et al [5] succeeded in the preparation of stable solutions of potassium and sodium tellurocyanate. 1, 4-dihydro-2-imino-3-telluraquinols were synthesized via the reaction of potassium tellurocyanate with 2-aminobenzyl iodide in DMSO solution. The cyclization reaction was described and the product characterization was reported elsewhere [6] .Physical studies of the new complexes have been reported. It was confirmed that these organotellurium compound which acts as donors the charge – transfer complexes are very interesting compounds due to their important applications in many pharmaceutical, biological and analytical fields [7-8]. Where the tellurium salts were used earlier in this century to treat syphilis, leprosy, and trypanosomiasis and the night sweats of pulmonary tuberculosis (anhydrotic effect) but these treatment are long obsolete [9] .
This paper is concerned with the reaction of new organotellurium compounds and their derivatives with DDQ antibacterial activities.

EXPERIMENTAL

(a) Preparation of complexes

All new organotellurium compounds used [compound 1-4] Scheme (1) through this work were prepared and purified using the procedures described in the literature [10], and the syntheses of charge transfer complexes were prepared by the reaction of

the tellurides with the corresponding DDQ. The general preparation route is illustrated by the following, as for preparation of DDQ complex with 2-imino-3-tellurapiperidine. A mixture of DDQ (0.01 mol.) and 2-imino-3-tellurapiperidine (0.02 mol.) in dry DMSO (50 ml.) was heated to reflux for 3 h.. A small quantity of dark –brown crystals was deposited from this reaction on cooling. The precipitate was washed with a small amount of H_2O and recrystallied from cyclohexane, m.p. 192-194ºC (compound I). Table 1 lists the charge – transfer complexes synthesized, together with their analytical data.



Scheme (1): The structure of the telluride's using in manuscript

(b) Conductivity Measurements

The measurements were determined in polymer research center by DC methods at room temperature. A sample of the $[C_4H_8N_2Te]^{++}[DDQ]_2^-$ complex was compressed into a disc of 10 mm diameter and 2 mm thickness. Two nickel electrodes were deposited on the disc by evaporation in vacuum (10^{-7} torr). Copper wires were attached by silver paint.

(c) Physical measurements

IR spectra were obtained using a Pye-Unicam SP3-300s instrument. All melting points were determined by a Gallenkamp melting point apparatus model and are uncorrected. Measurements of UV-vis spectra were obtained at room temperature by Pye-Unicam SP3-300S. ^{1}H NMR spectra were determined with a BRUKER FT NMR spectrometer (400 MHz) at Al-baath University (Syria) as solution in $CDCl_3$, using tetra methyl silane (TMS) as an internal standard. The elemental analyses of complexes were performed in CHNS-O Model Analyzer.

(d) Determination of antibacterial activity

(1) Primary screening

Primary screening for antibacterial activity of compounds [1-4] was carried out by disc diffusion technique [11]. Sterile discs containing 500 µg/disc were prepared. 24 h. old culture grown in nutrient broth (NB; Oxoid, England) containing 10^7 cfu.ml^{-1}(colony forming unit) was seeded to the Mueller-Hinton agar (Oxoid) plates. The prepared discs were placed on the surface at different positions and plates were incubated at 37 ºC for 24 h.; the results were recorded by measuring the average of diameters inhibition zone for each compound.

(2) Determination of minimum inhibitory concentrations (MIC)

The MIC of the compounds showing significant antibacterial activity against the organisms was determined by tube dilution technique. NB containing different concentrations of compounds varying from 0.1 – 125 µg/ml were used. Tubes containing 5ml both were inoculated with cultures containing 10^5 - 10^6 cfu.ml^{-1} and incubated at 37 ºC for 24 h. The results were recorded by visual inspection for turbidity. The MIC which was determined as the highest dilution of compound solution showing no turbidity.

(3) Determination of Minimum Bactericidal concentrations (MBC)

10 ml from each tube, showing no turbidity, was streaked on nutrient agar (oxoid) plates and incubated at 37 ºC for 24 h ..MBC was taken as a concentration which showed no bacterial growth after incubation.

Results And Discussion

The reaction of 2-imino-3-tellurapiperidine with DDQ in DMSO gave a complex of 1:2 stiochiometry, (Table 1). The change in their colour from yellow to dark brown as the distribution of the free electron over the nitrogen atom and tellurium atom and the tautomerizem. Therefore, a new band in the visible spectrum 300-1000 nm was observed at 25 ºC. This absorption is described to charge transfer complexes formed, since neither the telluride nor the π-acceptor DDQ alone absorbs in this region; this is due to the overlapping between charge – transfer n – π and π - π* transitions.

The IR spectra of all the complexes [compounds 1 – 4] show two bands between 465 and 530 cm^{-1} due to ט $_{as}$ (C-Te) and ט $_{s}$ (C-Te) which agree well with previous work [12-14]. The spectra of the complexes are quite similar to the superposition of the spectra of the components. There are slight shifts in frequency and some alterations in the intensity, which reflect the molecular association. The degree of charge-transfer of the complexes could be monitored by examination ofט (=NH, NH) for telluride, similar to ט (CN) in DDQ complexes [15]. We particularly noted shifts of +10 cm^{-1} for ט (CH_2),which seems reasonable for the more positive tellurium atom [16].

^{1}H NMR spectra of the complexes (table 2) are quite similar to the total signals of the components and which showed downfield signals at [δ 2.3 – 3.2] due to H_2C-5 and the triplet signals at [δ 3.45 – 4.0] due to H_2C-4, H_2C-6 these signals are almost appeared in same the position as the spectra of the compenats.

All complexes gave satisfactory elemental analysis and in agreement with the aretically calculated values for the expected compounds. However, the electrical conductivity of complex I, which was pressed at 11 tones to form a disc it conductivity was measured at various temperatures in the range 292 - 366 ºK, by a direct method. The variation of the resistivity with temperature was found to obey the usual behaviour of an intrinsic semiconductor [16-18] (Fig. 1).

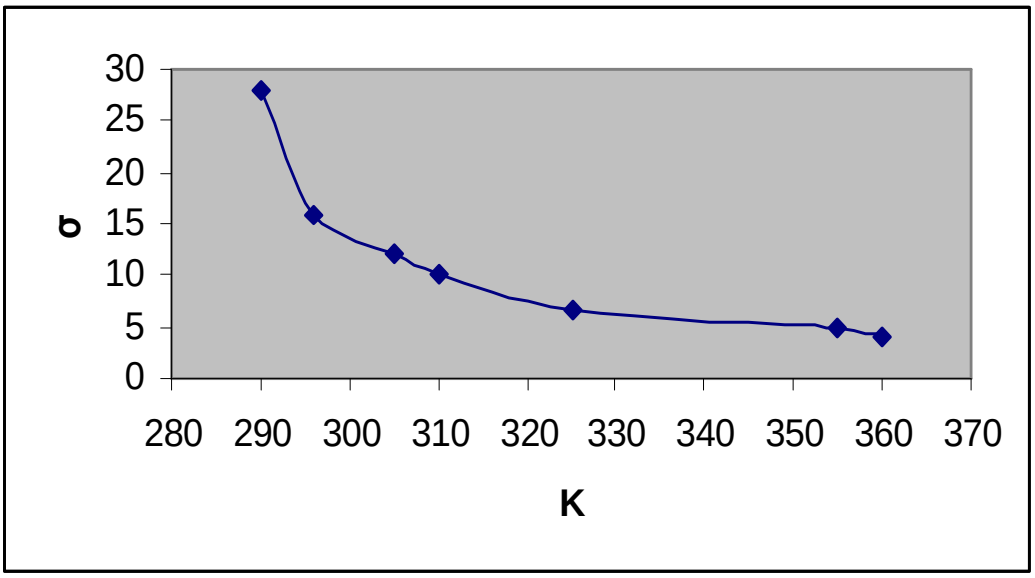


Fig.1 : The relation between resistivity (σ * 10^{-8} Ω cm) and temperatures(K)

Table 2 : ^{1}H-N.M.R data for the new organotellurium compounds

Comp.	Chemical shifts (ppm);TMS=0 PPM
I	2.3-2.9 (CH_2,m,2H)3.45 (CH_2,t,4H)4.8 (NH,s,2H)
II	2.3-3.05 (CH_2,m,2H) 4.0 (CH_2,t,4H) 5.7 (NH,s,2H)
III	2.35-3.15 (CH_2,m,2H) 3.6 (CH_2,t,4H) 4.9 (NH,s,2H)
IV	2.4-3.2 (CH_2,m,2H) 3.6 (CH_2,t,4H) 4.9 (NH,s,2H)

Antibacterial activity

Antibacterial activities show all the complexes were subjected to a primary screening for their antibacterial activity in *vitro* against (4) Gram-positive and (15) Gram-negative bacteria. All of them showed a significant activity against the bacteria tested; these complexes showed a marked activity against several Gram-negative bacteria. This finding aggresses with the results reported by Turner et al [19]. Mechanism of tellurium toxicity is interpreted in term an interaction with the reduced thiols (RSH) [20]. The MIC of complexes was in the range of 0.1 to 125 µg/ml depends on the species of bacteria. The MBC in most of the cases was higher than their MIC.

Table 2: Screening of compound :(I-IV)
For antibacterial activity in *vitro* (zones of inhibition in millimetres)

Compounds	I	II	III	IV
Gram-positive				
Staphylococcus aureus (NCTC 6571)	13	12	14	13
Staphylococcus aureus	10	11	12	14
Bacillus pumilus (NCTC 8241)	16	14	12	14
Bacillus subtilis	14	11	15	10
Gram-negative				
Escherichia coli (NCTC 5933)	17	16	15	17
Escherichia coli	13	14	12	15
Pseudomonas aeruginosa (ATCC 27853)	15	13	13	14
Pseudomonas aeruginosa	13	12	12	15
Salmonella typhi	18	18	20	22
Salmonella paratyphi A	10	12	12	15
Shigella dysenteriae	13	10	16	18
Klebsiella pneumoniae	12	15	11	12
Serratia marescens	20	12	21	18
Proteus vulgaris	19	15	18	16
Acinetobacter Aci 108(450373)	18	19	16	18
Acinetobacter haemolyticus Aci 014(320565)	13	10	12	12
Acinetobacter baumannii Aci 001(180265)	18	14	14	13
Acinetobacter lwoffii Aci 017(320568)	23	24	24	22
Acinetobacter calcoaceticus Aci 013(320564)	15	13	10	18

Table 3 : Minimum inhibitory concentration (MIC) values and minimum bactericidal concentration (MBC) in µg/ml for compounds (I-IV)

Compound	I		II		III		IV	
	MIC	MBC	MIC	MBC	MIC	MBC	MIC	MBC
Gram-positive								
*Staphylococcus aureus(*NCTC 6571)	50	75	25	50	25	50	25	50
Staphylococcus aureus	75	100	50	75	25	25	5	10
*Bacillus pumilus (*NCTC 8241)	1	5	5	10	5	10	5	10
Bacillus subtilis	5	10	10	15	0.1	0.5	25	50
Gram-negative								
Escherichia coli (NCTC 5933)	10	15	5	10	5	10	0.5	1
Escherichia coli	100	125	10	15	50	75	25	50
Pseudomonas aeruginosa (ATCC27853)	10	15	25	50	25	50	25	50
Pseudomonas aeruginosa	50	75	25	50	75	100	25	50
Salmonella typhi	5	10	5	5	0.1	0.5	0.1	0.5
Salmonella paratyphi A	25	50	25	50	25	50	15	20
Shigella dysenteriae	25	50	75	100	25	50	25	50
Klebsiella pneumoniae	25	50	10	15	25	50	50	75
Serratia marescens	10	15	25	50	15	20	25	25
Proteus vulgaris	1	5	15	20	1	5	5	10
Acinetobacter Aci 108(450373)	15	20	25	50	50	50	15	20
Acinetobacter haemolyticus Aci 014(320565)	25	50	125	125	25	50	10	15
Acinetobacter baumannii Aci 001(180265)	25	50	25	50	50	75	75	100
Acinetobacter lwoffii Aci 017 (320568)	5	10	5	5	15	20	15	20
Acinetobacter calcoaceticus Aci 013 (320564)	0.1	0.5	15	20	25	50	1	5

Conclusions

New hetrerocyclic tellurium compounds based on 2-imino-3-tellurapiperidine have been synthesized and found to form charge-transfer complexes with DDQ and have antibacterial activity.

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دراسة عن معقدات نقل الشحنة بين بعض مركبات التلوريوم الجديدة مع ثنائي كلوروثنائي سيانوكوينون وتطبيقاتها في الفعالية البكتيرية

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الخلاصة

استخدمت مشتقات جديدة للتلوريوم كمانحات لتكوين معقدات (مانح–مستقبل) مع 2,3–ثنائي كلورو–5,6–ثنائي سيانوبنزوكوينون(DDQ) تم متابعة معقدات انتقال الشحنة $\pi^* \longrightarrow n$ طيفيا في محلول ثنائي مثيل سلفوكساید . المشتقات الجديدة المحضرة بحصيلة جيدة نقيت وشخصت باستخدام تحاليل العناصر الدقيق , واطياف الاشعة فوق البفسجية–الاشعة المرئية , الاشعة تحت الحمراء, والرنين النووي المغناطيسي البروتوني, والتوصيلية للصلب.
أظهرت معقدات 2:1 الصلبة أدلة تؤكد امتلاكها لصفات اشباه الموصلات. كما اظهرت المشتقات الجديدة للتلوريوم فعالية بايولوجية.