Synthesis and Structural Studies of Some Transition Metal Complexes of 5- phenyl-1,3,4 – Oxadiazole-2- thioethyl Carbanate

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Abstract

New complexes of cobalt (II), palladium (II), and platinium(II) with 5-phenyl- 1,3,4-oxadiazole-2- thioethylcarbanate (OXE) have been prepared and characterized by elemental analysis, IR,UV-Vis spectra, magnetic susceptipibility, and conductivity measurements. Probable structures of the prepared complexes have been reported.

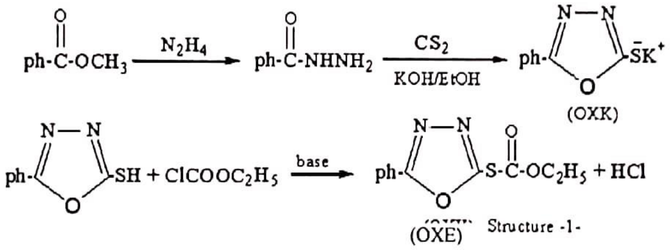
Introduction

The aromatic oxadiazole nucleus form an important class of biologically active compound with a varity of pharmacologic actions especially –3- thio derivatives are very important because they contain the N-C=S moiety (1,2). The presence of the soft atom besides the hard atom in this thioamide " keeping aside the effects of the reminder of the molecule containing it". Althought these molecules with ethyl ester to be apotent ligands with a wide diversity and versatity toward the transition elements (3,4), which is the key for the biological importancet beside other utilities and applications (5).

Experimental

Materials and physical measurements: The chemicals used in this work were of the highest purity available (Fluka).The melting point were recorded using gallenkamp (visual) melting point apparatus. Infrared spectra were obtained using Pye- Unicom SP-300 and Perkin- Elmer 1310, spectrophotometers in the range (4000-200) cm^{-1}. Perkin – Elmer Lambda9 and shimadzu UV-160 spechophotometers have been used for uv- visible spectra in the range 200-1100 nm. Solution was prepared in DMF and 10mm silica cells then microanalytical dada were obtained using perkin- Elmer 340B elemental analyzer. Magnetic susceptibility measurements were measured using Bruker magnet BM6. Conductivity measurements have been done by WTW conductivity meter Philips apparatus.

Preparation: The ligand (potassium-5- pheyl-2- thio -1,3,4-oxadiazole) (OXK) was prepared according to young and wood method [6].While the ligand 5-phenyl -1,3,4-oxadiazole -2-thioethyl carbonate (OXE) was prepared according to the literature method (7), using pyrdine instead of sodium carbonate as a base and solvent which shows to give better yield.



Structure -1-

The physical properties and infrared spectra are given in table (1and 2)

[$CoCl_2$ (OXE)].H_2O: Dichloro (5-phenyl – 1,3,4- oxadiazole –2-ethyl thio carbonate) cobalt (II), was prepared by the addition slowly of cobalt chloride (0.5 mmole) to (1.1 mmole) of heterocyclic ligand (OXE) solution , using ethanol as solvent. The mixture was refluxed and stirred for 30 min, then cooled to room temperature, blue crystals were formed. It was recrystallized from ethanal .The product was characterized by using its elemental analysis, IR, UV,- vis, magnetic susceptibility and conductivity measurements , See tables (1-3) .

[$PdCl_2$ (OXE)].H_2O: Dichloro(5- phenyl- 1,3,4- oxadiazole- 2-ethylthiocarbonate) palladium (II), was prepared in similar manner to the above complex using dichloro bis(benzonitril) palladium (II) . The orange precipitate was isolated and purified with a mixture of ethanol acetone , then dried under vacuum . It was characterized by similar techniques mentioned in cobalt complex and the results are shown in tables (1-3) .

[$PtCl_2$ (OXE)H_2O]$_2$ .H_2O: Di-μ- chlorobis cholro (5- phenyl- 1,3,4- oxadiazole- 2- etheyl thio carbonate) aquo platinium (II) , was prepared in similar manner to the previous complexes using potassium hexachloroplatinate . The yellow crystals were obtained after cooling the mixture to room temperature,which were soluble in DMF solvent.The product was identified by similar techniques used in the previous complexes and the results are shown in tables (1-3).

Results and Discussion

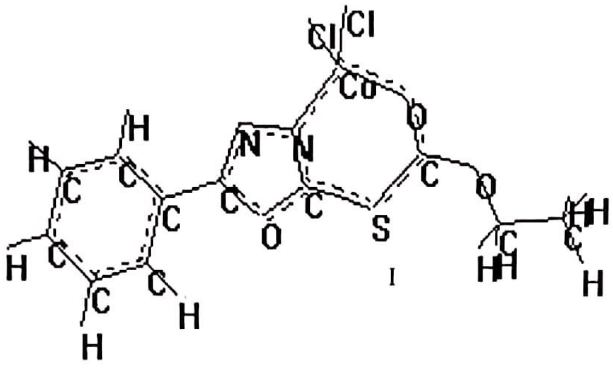
These stable complexes were isolated with the above ligand .Based on the microanalyical data, their general formula can be depicted as the neutral species [MCL_2 (OXE)].H_2O, where M= Co , Pd and the dimeric complex [$PtCl_2$ (OXE)(H_2O)] $_2$ .H_2O.Table (1). OXE is abidentate ligand, see the structure (1).

So it is expected that i.r measurements are highly infermative . The charactristic frequencies of free ligand and its metal complexes were readily assigned based on comparison with the literature (8,9) . The i.r spectra data of OXE and its complexes with their respective assignments are shown in table (2) . OXE exhibited the diagnostic (C=O) at 1770 cm-^{1}, υ_{cH} aliphatic at 2980 cm^{-1} and C-O ester at 1215 cm^{-1} indicative of the ethyl formate bonded to the thio atom (10, 11) shifts to lower frequency of 70 cm^{-1} was observed for OXE complexes which lend a support to the participation of carbonyl – oxygen in coordination . The two bonds of OXE at 1496 and 1569 cm^{-1} (which originate from thioamide band I), shifted to lower frequency upon complexation indicative of the coordint through nitrogen. In addition to oxygen atom of the other diagnostic bands are ; (1) . The 3450 and 1620 cm^{-1} bands belonging to coordinated water of platinium complex and presence of water molecules in crystal lattice of three complexes .(2) The weak bands was noticed at 350, 330; 320 and 290: 350 for complexes I, II and III respectively which can be characterized as belonging to symmetric and asymmetric frequencies of two chloride atoms coordinated in cis position (8) .

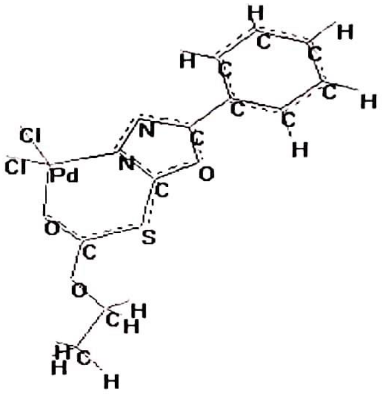
The magnetic measurements show the cobalt ion in its blue complex to be paramagnetic with d^7 configuration in distorted tetrahedral enviroment (12,13) . This suggestion is supported by the number of maxima observed in uv – vis. spectrum of the complex, which show 3 maxima and be assigned to the transition $^4A_2g \rightarrow {}^4T_2g$, $^4A_2g \rightarrow {}^4T_1g_{(F)}$ and $^4A_2g \rightarrow {}^4T_1g_{(p)}$, table (3) . The racah parameter $B^{`}$, B and the value of 10 Dq where calculated by reference to Tanaba – Sugano diagram for d7 configuration (12,14). The conductivity measurements in DMF show the complex to be non- conducting.

The orange palladium OXE complex shows strong change transfer bands which was extended to the visible region , so the ligand field bands could not be established easily. Neverthless, two weak bands at 23,000 cm^{-1} and at 35,900 cm^{-1} may be assigned to the transition $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1Eg$, respectively, for spin paired d^8 squar planner configuration with magnetic moment value of (0.00 BM) . This assignment was made by reference to known palladium complexes with squar planar stereochemistry. This is in good agreement with published data (15) . The conducting measurements indicate the non- electrolyte behavior of the complex. Results are given in table (3).

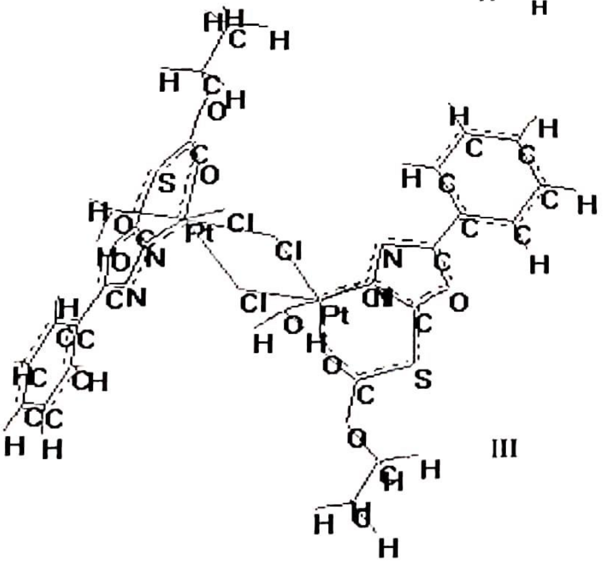
On inspection of the dimeric platinium complex, the present work reveals that the first charge- transfer band appeared in this complex at about 36,000 cm^{-1}, is highly reduced in intensity and became shoulders to the second band at about 43,200 cm^{-1}. This assumes the reduction to the divalent state of pt (IV) which gave rise to the stronge CT bands in the spectra. Secondly, it is known from the spectra of distorted octahedral complex that a component of low symmetry in the ligand field manifests itself in the splitting of orbitally degenerate terms, and this band splitting takes place in the trans and not in the cis isomer (12,16). The weak bands (15, 966 & 23,482) cm^{-1} of the present Pt (II) complex corresponds in average position and in total intensity , to the band at (19,7185) $cm^{-1}$of Pt (IV), this is agood evidence for the prepared complex with central atom in the bivalent state (16) . The magnetic moment shows the platinium (II) ion to be (2.7BM) with d^8 configuration in a distorted oh environment. The conductivity measurements indicate the non- conducting behavior of the compound.The proposed structure of the prepared complexes are drawn as follows using **Hyperchem.6 Program:**



I



II



III

Conclusion

The bidentet heterocyclic ligand (OXE) was reacted with a preparative metal salt in ethanol,different colored complexes were obtained, they were studied and identified by CHN,spectroscopic,magnetic and conducting measurements,which have been non-electrolyte. All complexes indicative of coordination through nitrogen and oxygen atoms show to give different structure formulation .

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Table (1) Physical data for OXE and its complexes

Compounds	**colour**	**Solven**	**melting Point C**	**Yield %**	**Element analysis Found (calc.)**		
					C%	N%	H%
OXE	white	ethanal	129-130	60	-	-	-
$[CoCl_2(OXE)].H_2O$ I	blue	ethanal	189_d	52	33.9 (33.25)	6.52 (7.05)	2.01 (2.77)
$[PdCl_2(OXE)].H_2O$ II	Orange	ethanal	144_d	25	28.01 (29.70)	6.50 (6.30)	2.31 (2.47)
$[PtCl_2(OXE)H_2O]_2.H_2O$ III	yellow	ethanal	163_d	20	25.9 (24.34)	5.00 (5.61)	2.01 (2.41)

Table (2) Selected infrared bands for the prepared OXE compounds, cm^{-1}

Componds	υC=O	I ∫NH+C=N	II υC=N+C=S	III υN..C...S	IV ʺC-S	ʺN-N	ʺC-O-C	υCH	υc-0 ester	υoH	υM-Cl
OXK	--	1490 1552	1415	929	770	1445	1138	--	--	--	--
OXE'	1770	1496 1569	1309 1349	935	770	1448	1100	2980	1215	--	--
I	1700	1485 1585	1335 1370	920 970	770	1450	1080		1180	3435	335 320
II	1700	1488 1555	1310 1360	920 965	770	1450	1085		1189	3450	330 320
III	1700	1490 1565	1335 1370	925 993	770	1458	1080		1180	2440	350 292

Table (3) Electronic spectral data of OXE complexes and their probable assignments,conductivity μscm^{-1} and magnetic moment (B.M) in DMF solvent .

Compounds	Bands cm^{-1}	Assignment	B cm^{-1}	Dq/B	B	β	10Dq	Cond μscm^{-1}	μ_{eff}B.M
I	16040 5533 15750	$^{4}A_{2}g\rightarrow{}^{4}T_{2}g$ $^{4}A_{2}g\rightarrow{}^{4}T_{1}g_{(f)}$ $^{4}A_{2}g\rightarrow{}^{4}T_{1}g_{(p)}$	1128	0.49 CB	6 9 2	0.6	16040	70	4.77
II	23000 25560 323oo 35900	$^{1}A_{1}g\rightarrow{}^{1}B_{1}g$ $^{1}A_{1}g^{1}\rightarrow Eg$ CT CT					32000	42	0.00
III	15966 23482 36000 43200	$^{1}A_{1}g\rightarrow{}^{1}T_{2}g$ $^{1}A_{1}g\rightarrow{}^{1}T_{1}g$						3.0	2.7

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد 18 (3) 2005

تحضير ودراسة تركيبية لمعقدات الكوبلت (II)، البلاديوم (II)، والبلاتين(II)، مع الليكاند 5- فنيل -1، 3، 4- اوكسادايازول – 2- ثايواثيل كارباميت

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الخلاصة

تم في هذا البحث تحضير ودراسة تركيبية لمعقدات الكوبلت (II)، البلاديوم (II)، والبلاتين(II)، مع الليكاند 5- فنيل -1، 3، 4- اوكسادايازول – 2- ثايواثيل كارباميت (OXE) وتشخيصها بطرائق التحليل الدقيق للعناصر، الاشعة تحت الحمراء، الاشعة فوق البنفسجية – المرئية، القياسات المغناطيسية والتوصيلية الكهربائية. تم اقتراح التراكيب المحتملة للمعقدات المحضرة الجديدة.