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Homobimetallic Complexes of Platinum(II) Group Metals with Sulphur Containing Ligands $R_2C = CR_2$ (R = 5-Phenyl-1,3,4-Oxadiazole-2-Thiol; 4,5-Diphenyl-1,2,4-Triazole-3-Thiol or Mercaptobenzothiazole)

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Homobinuclear complexes of the type $[Cl_2MR_2C{=}CR_2MCl_2]$ [M = Ni(II), Pd(II) or Pt(II) and R = 5-phenyl-1,3,4-oxadiazole-2-thiol; 4,5-diphenyl-1,2,4-triazole-3-thiol or mercaptobenzothiazole], have been prepared by the reaction of newly prepared sulphur containing ligands of the type $R_2C{=}CR_2$ with the appropriate metal salts of Ni(II), Pd(II) or Pt(II). The complexes have been characterized on the basis of their CHN elemental analysis, molar conductivity, room temperature magnetic moment, I.R. and electronic spectra. Octahedral enviroment around Ni(II) while square-planar geometry around Pd(II) or Pt(II) have been deduced on the basis of magnetic and spectral studies.

Key Words: Homobimetallic complexes, Platinum(II), Sulphur.

INTRODUCTION

Transition metal complexes of sulphur donor ligands have been a subject of current interest, not least because of the biochemical significance of such species[1–3]. Many platinum group metal complexes have been found to catalyze important chemical reactions involving unsaturated organic molecules. The existence of a vacant coordination site is an essential property of homogeneous catalysis, since it allows organic substrates to enter the coordination sphere of the metal atom[4, 5].

The coordination compounds of 5-methyl-1,3,4-thiadiazole with some group VII metals such as Ru(III), Rh(III), Os(III) and Ir(III) have been prepared and studied[6]. Recently some novel 1,3,4-oxadiazole derivatives and their anti-inflammatory activity have been reported[7]. More recently several palladium complexes derived from 2,5-diphenyl-1,3,4-oxadiazole and their reactivity against nucleobase models[8] and complexes of 5-phenyl-1,3,4-oxadiazole-2-thione with Ni(II), Pd(II) and Pt(II) have been reported[9] as complexes of Zn(II), Pd(II) and Hg(II)

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with 1,2,4-triazole derivative[10]. As a part of our interest in the coordination chemistry of heterocyclic ligands, we wish to report here the synthesis of some new heterocyclic ligands and their complexes which have besides the two or three hetero atoms of the five membered ring, another potential binding site, *i.e.*, the sulphur atom.

EXPERIMENTAL

All chemicals used were of high purity. Analyses of ligands and complexes were carried out using a CHN elemental analyzer model 1100 (Carlo Erba). The metal content was estimated spectrophotometrically using Shimadzu AA 670 spectrophotometer. Melting points and decomposition temperatures were determined on a Buchi 510 melting point apparatus and were uncorrected. Infrared spectra within the 4000–200 cm^{-1} range were recorded on a Perkin-Elmer 580B spectropotometer, calibrated with polystyrene. The samples used were in the form of KBr or CsI discs. Electronic spectra were obtained with a Shimadzu UV/Vis. recording UV 160 spectrophotometer at room temperature. The measurements were recorded using a concentration of 10^{-3} M of the complex in acetonitrile. The magnetic moments were carried out at 25°C on the solid state by Faraday's method using Brucker BM6 instrument . Conductivities were measured using a conductivity meter model PCM3-Jenway. These measurements were obtained using dimethyl sulphoxide or acetonitrile over a concentration of 10^{-3} M at 25°C.

Synthesis

The groups (R) of the ligands $R_2C = CR_2$; 5-phenyl-1,3,4-oxadiazole-2-thiol (oxadiazole); 4,5-diphenyl-1,2,4-triazole-3-thiol (triazole) and mercaptobenzothiazole **(Scheme 1)** were prepared by a standard method[11].

The ligands ($R_2C{=}CR_2$): 1,1,2,2-tetrakis-(oxadiazole, triazole or mercaptobenzothiazole)ethylene were prepared by using the following methods.

1,1,2,2,-tetrakis oxadiazole ethylene (L)

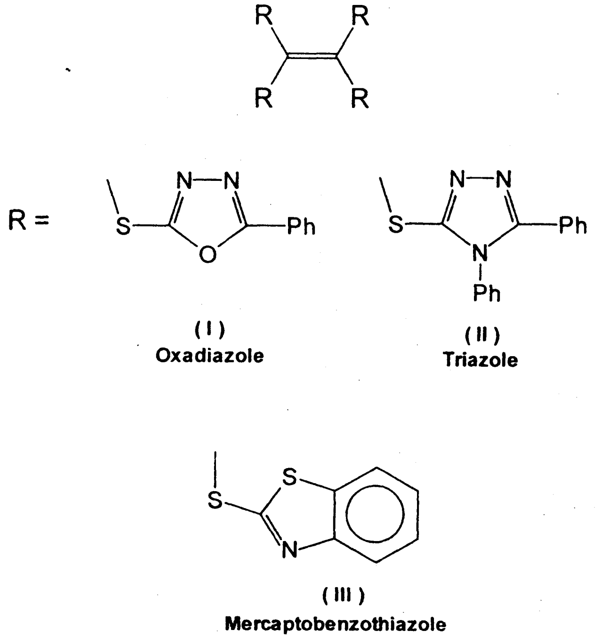
1,1,2,2-Tetrachloroethylene was heated under reflux for *ca.* 5 h with an equivalent amount of oxadiazole and KOH in ethanol (40 mL). After cooling to room temperature, KC1 was removed by filtration. The resulting solution was reduced in volume to about half of its original volume and on cooling a white solid was obtained which was filtered off, dried and recrystallized from *n*-propanol. The other ligands were prepared in a similar manner.

[M_2LCl_4] complexes: The complexes were prepared according to the following general procedure:

A solution of the ligand (1 mmol) in ethanol (15 mL) was added to a solution of $NiCl_2{\cdot}6H_2O$ or K_2MCl_4 (M = Pd or Pt) (2 mmol) in water (10 mL). A rapid formation of a precipitate was observed in the case of Pd or Pt while with Ni, the precipitation took longer time. The mixture was stirred under reflux for *ca.* 1 h to ensure completion of the reaction. The solid thus obtained was filtered off, washed with warm water, ethanol then ether and dried under vacuum for several hours.

RESULTS AND DISCUSSION

Treatment of tetrachloroethylene with a sufficient amount of oxadiazole, triazole or mercaptobenzothiazole in the presence of KOH results in the formation of the corresponding ligands **(Scheme-1).** These are new ligands; their physical properties are listed in Table-1.



Scheme 1. Ligands ($R_2C{=}CR_2$) used in tthe present study

TABLE-1
PHYSICAL PROPERTIES OF THE FREE LIGANDS

Seq.	Ligand (colour)	m.p. (°C)	Analysis: Found (Calcd.) %			Selected IR bands (cm^{-1})			
			C	H	N	ν(C—S)	ν(C=N)	ν(C–O–C)	ν(C=C)
(I)	Oxadiazole (white)	280	55.46 (55.74)	2.88 (2.73)	15.5 (15.30)	670	1620	1290	1660
(II)	Triazole (white)	221[a]	67.66 (67.44)	3.91 (3.88)	16.17 (16.28)	650	1625	—	1660
(III)	Merc. (white)	217	63.90 (63.83)	3.62 (3,55)	10.01 (9.93)	660	1620	—	1650

[a]Compound melts with decomposition.

The complexes can be prepared directly by treating the above ligands with either $NiCl_2 \cdot 6H_2O$ or K_2MCl_4 (M = Pd or Pt) in boiling aqueous ethanol in a molar ratio 1 : 2. The isolated complexes and their physico-chemical properties are listed in Table-2. In general, the complexes were slightly soluble in halogenated solvents but rather more soluble in acetonitrite, N,N-dimethyl formamide and dimethyl suphoxide. The molar conductances in 10^{-3} M DMF solution are in the 15–26 ohm^{-1} mol^{-1} cm^2 range indicating the nonelectrolytic nature of the complexes. This is consistent with the stoichiometry assumed for the complexes on the basis of analytical data.

TABLE-2
PHYSICAL PROPERTIES AND MOLAR CONDUCTANCE OF THE COMPLEXES

Seq.	Ligand (colour)	m.p. (°C)	Analysis, found (calcd.) %				Λ_M (ohm^{-1} cm^2 mol^{-1})
			C	H	N	M	
1	$[Ni_2(\mathbf{I})Cl_4]$ (dark yellow)	338[a]	41.00 (41.21)	1.96 (2.02)	11.30 (11.31)	11.75 (11.82)	18
2	$[Pd_2(\mathbf{I})Cl_4]$ (dark yellow)	335	37.49 (37.53)	1.86 (1.89)	10.25 (10.30)	19.56 (19.59)	25
3	$[Pt_2(\mathbf{I})Cl_4]$ (brown)	350	32.24 (32.28)	1.55 (1.58)	8.85 (8.86)	b	20
4	$[Ni_2(\mathbf{II})Cl_4]$ (dark yellow)	360[a]	53.76 (53.91)	3.03 (3.09)	13.00 (13.01)	9.01 (9.09)	30
5	$[Pd_2(\mathbf{II})Cl_4]$ (orange)	320[a]	54.00 (54.08)	3.09 (3.11)	13.00 (13.05)	16.51 (16.53)	29
6	$[Pt_2(\mathbf{III})Cl_4]$ (brown)	360	44.45 (44.56)	2.51 (2.56)	10.70 (10.74)	24.91 (24.94)	32
7	$[Ni_2(\mathbf{III})Cl_4]$ (khaki)	360[a]	43.71 (43.74)	2.40 (2.43)	6.75 (6.80)	14.23 (14.26)	30
8	$[Pd_2(\mathbf{III})Cl_4]$ (red)	302	39.12 (39.17)	2.15 (2.18)	6.06 (6.09)	23.10 (23.15)	28
9	$[Pt_2(\mathbf{III})Cl_4]$ (dark red)	360	32.80 (32.85)	1.80 (1.82)	5.09 (5.11)	b	34

[a]Complexes melt with decomposition.; [b]Not measured.

The palladium and platinum complexes are diamagnetic (Table-3) while nickel complexes have magnetic moments at room temperature ranging between 3.0 to 3.3 B.M.

The ligands dose not show any ν(SH) band in the region of 2600–2500 cm^{-1}, in which this stretching frequency generally expected[12]. The characteristic bands in the infrared spectra of the free ligands occur at 1660, 1620, 1290 and 670 cm^{-1} due to the stretching vibrations ν(C=C), ν(C=N), ν(C—O—C) and ν(C—S), respectively[13]. In the nickel complexes of these ligands, it was found that the bands ν(C—O—C) and ν(C—S) (oxadiazole), ν(C=N) and ν(C—S) (triazole), ν(C=N) and ν(C—S) attached to the double bond of the mercaptobenzthiazole show lowering in frequencies, indicating that these bands are involved in the coordination while in the Pd(II) complexes of all ligands, only the ν(C—S) band

TABLE-3

ELECTRONIC, INFRARED SPECTRAL BANDS (cm^{-1}) AND MAGNETIC MOMENTS (B.M.) OF THE COMPLEXES

Complex[a] seq.	λ_{max} (nm), (E_{max} M^{-1} cm^{-1})	ν(C—S)	ν(C=N)	ν(C—O—S)	ν(Ni—N)	ν(M—S)	ν(M—Cl)	ν(M—O)	μ_{eff} (B.M.)
1	770 (11000), 525 (9000), 392 (1600)	650	1620	1250	440	380	340	500	3.0
2	285 (17980), 440 (6500)	640	1620	1290	—	375	330 295	—	Dia
3	323 (5280), 367 (4000), 420 (14650)	650	1620	1290	—	370	330 290	—	Dia
4	779 (8000), 545 (12000), 345 (17200)	640	1600	—	440	380	340	—	3.3
5	260 (16820), 348 (7500), 43 (15570)	630	1620	—	—	—	330 290	—	Dia
6	375 (16650), 391 (15500)	635	1620	—		—	330 300	—	Dia
7	779 (15000), 569 (11000), 423 (12600)	640	1595	—	430	—	340	—	3.2
8	348 (9000), 381 (9980), 504 (15110)	655	1620	—	—	—	330 295	—	Dia
9	290 (3000), 400 (15000), 548 (12690)	650	1590	—	435	—	340 295	—	Dia

has been involved in coordination (Table-3). The infrared of Ni(II) complexes show new bands at 500, 440 and 380cm^{-1}, assigned to ν(Ni—O)[14], ν(Ni—N)[15] and ν(Ni—S)[16], respectively. The IR spectra of the Pd(II) and Pt(II) complexes show bands within the range 330–305 and 350 cm^{-1}, which are tentatively assigned to ν(M—Cl) and ν(M—S)[18], respectively. The band at 330–305 cm^{-1} is splitted into two bands at 330 and 305 cm^{-1} and this can be taken as evidence for a square planer *cis*-configuration of these complexes[3].

In order to obtain some information about the coordination properties of the metal ions, the electronic spectra have been recorded. The tentative assignments of the absorption bands from the electronic spectra of the complexes are reported in Table-3.

The electronic spectra of Ni(II) complexes show three d-d transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$, $3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$, $^3A_{2g} \rightarrow {}^3T_{2g}(P)(\nu_3)$, indicating the octahedral geometry of the Ni(II) complexes[19]. The d-d bands from the spectra of Pd(II) and Pt(II) complexes, having low intensities were assigned according to the literature data[19] due to the transitions $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ or charge transfer transition; they suggest a square planar geometry around the metal ion[20].

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