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SYNTHESIS, CHARACTERISATION AND ANTIFUNGAL ACTIVITY OF Ru(III) COMPLEXES WITH HETEROCYCLIC DITHIOCARBAMATES

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ABSTRACT

Several new hexa-coordinated ruthenium(III) complexes of the type [$RuX_2(EPh_3)_2(LL')$], (X = Cl or Br; E = P or As) [where LL' = morpholinedithiocarbamate (Morphdtc), piperidinedithiocarbamate (Pipdtc) and piperazinedithiocarbamate (Pzdtc) have been synthesised. In all these complexes the heterocyclic dithiocarbamates behave as a uninegative bidentate (SS) chelating ligand. It has been observed that the incoming ligand replaces a halide, a tertiary phosphine/arsine and methanol from the starting complexes. All the complexes have been characterised on the basis of analytical and spectroscopic data. The new complexes showed a reasonable amount of antifungal activities.

INTRODUCTION

The chemistry of metal dithiocarbamates has been investigated due to their wide applications, interesting

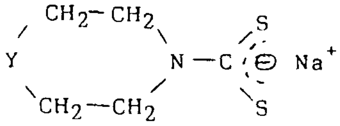

Fig. 1. Dithiocarbamate Ligands

where Y = O, Morphdtc
= CH_2, Pipdtc
= NH, Pzdtc

structural properties and biocidal activities[1-3]. Despite considerable interest in the transition metal dithiocarbamate complexes,[4-9] relatively little work has so far been done on the preparation and characterisation of the mixed ligand complexes of ruthenium(III) with heterocyclic dithiocarbamates. We report here the synthesis, characterisation and some antifungal activities of triphenylphosphine complexes of ruthenium(III) with heterocyclic dithiocarbamates. The dithiocarbamates used in this study are of the type shown in Fig. 1.

EXPERIMENTAL

All reagents used were Analar or of chemically pure grade. All solvents were freshly distilled before use. IR spectra were recorded in KBr on a Perkin-Elmer 597 IR grating spectrophotometer in the range 4000-200 cm^{-1}. Electronic spectra were obtained from dichloromethane solutions on a Hitachi-Elmer model 20/200 spectrophotometer.

EPR spectra of powdered samples were recorded with a Bruker ER-200 EPR spectrometer at X-band frequencies. Cyclic voltammetric studies were carried out in acetonitrile using a glassy-carbon working electrode and the potentials were referenced to an Ag/AgCl electrode. Microanalyses were performed at the Research and Development Laboratory, Hindustan Photo Film Industry, Ooty. Melting points were recorded on a Mettler Fb51 instrument and are uncorrected. The starting complexes $[RuCl_3(PPh_3)_3]$[10], $[RuCl_3(AsPh_3)_3]$[11], $[RuBr_3(AsPh_3)_3]$[12], $[RuBr_3(PPh_3)_2MeOH]$[13] and the ligands[14] were prepared by the methods reported in the literature.

The fungus Fusarium sp. was grown on a potato-dextrose agar (PDA) medium and purified by the single spore isolation technique. Seven day old cultures were used for the study. Several solutions of different concentration (ppm) of ruthenium(III) complexes and of the ligands were prepared in DMSO. The percentage inhibition of the complex against the fungal growth were then calculated.

Preparation of $[RuX_2(EPh_3)_2(LL')]$ (X = Cl or Br; E = P or As; LL' = Morphdtc, Pipdtc, Pzdtc)

To a solution of $[RuCl_3(PPh_3)_3]$ (0.12 g; 0.125 mmol) in benzene (20 mL) the appropriate sodium salt of piperidine dithiocarbamate (0.020 g; 0.125 mmol) (1:1 mole ratio) in methanol (5 mL) was added. The solution was heated under reflux for 5 h. After concentrating the solution to about 2 mL, the product was separated by the addition of a small quantity of hexane. The compound was recrystallised from CH_2Cl_2/n-hexane and dried under vacuum. All other complexes were prepared using similar procedures. Yield : 70%; 0.072g.

RESULTS AND DISCUSSION

The new complexes having the general molecular formula $[RuX_2(EPh_3)_2(LL')]$ have been obtained from the reactions of $[RuX_3(EPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ with various dithiocarbamates. The analytical data given in Table I are in good agreement with the molecular formula arrived at for all the complexes. All the complexes are coloured and are quite stable in air.

$[RuX_3(EPh_3)_3]$
or + Sodium salt of Dithiocarbamates $\xrightarrow[\text{Reflux}]{\text{Benzene}}$
$[RuBr_3(PPh_3)_2(MeOH)]$
$[RuX_2(EPh_3)_2(LL')]$

where LL' = Dithiocarbamates

IR Spectra

In all the new complexes the $\nu C{=}N$ and $\nu C{=}S$ stretching frequencies of the dithiocarbamates fall in the range 1460-1485 cm^{-1} and 980-1000 cm^{-1} (Table II) indicating the coordination through the two sulphur atoms of dithiocarbamate. Besides, the complexes exhibited only one strong band at ~ 1000 cm^{-1} supporting the bidentate nature of the dithiocarbamate moiety. A doublet is expected

Table I. Analytical Data of Ru(III) Complexes

Sl. No.	Complex	Yield %	Empirical Formula	Colour	mp °C	Elemental Analysis Found (Calculated)% C	H	N
1.	$[RuCl_2(PPh_3)_2(Pipdtc)]$	70	$C_{42}H_{40}NS_2P_2Cl_2Ru$	Green	130	58.89 (58.90)	4.67 (4.65)	1.63 (1.62)
2.	$[RuCl_2(AsPh_3)_2(Pipdtc)]$	63	$C_{42}H_{40}NS_2As_2Cl_2Ru$	Brown	178	53.42 (53.85)	4.24 (4.60)	1.48 (1.44)
3.	$[RuBr_2(AsPh_3)_2(Pipdtc)]$	66	$C_{42}H_{40}NS_2As_2Br_2Ru$	Brown	142	48.80 (49.00)	3.87 (3.82)	1.35 (1.36)
4.	$[RuBr_2(PPh_3)_2(Pipdtc)]$	71	$C_{42}H_{40}NS_2P_2Br_2Ru$	Brown	155	53.34 (53.29)	4.23 (4.02)	1.48 (1.45)
5.	$[RuCl_2(PPh_3)_2(Pzdtc)]$	70	$C_{41}H_{39}N_2S_2P_2Cl_2Ru$	Pale green	160	57.42 (57.26)	4.55 (4.43)	3.26 (3.07)
6.	$[RuCl_2(AsPh_3)_2(Pzdtc)]$	62	$C_{41}H_{39}N_2S_2As_2Cl_2Ru$	Brown	179	52.08 (52.03)	4.12 (4.12)	2.96 (2.98)
7.	$[RuBr_2(AsPh_3)_2(Pzdtc)]$	74	$C_{41}H_{39}N_2S_2As_2Br_2Ru$	Brown	173	47.59 (47.67)	3.77 (3.57)	2.71 (2.66)
8.	$[RuBr_2(PPh_3)_2(Pzdtc)]$	77	$C_{41}H_{39}N_2S_2P_2Br_2Ru$	Brown	142	52.02 (52.33)	4.12 (4.07)	2.96 (2.93)
9.	$[RuCl_2(PPh_3)_2(Morphdtc)]$	80	$C_{41}OH_{38}NS_2P_2Cl_2Ru$	Pale green	159	57.36 (57.49)	4.43 (4.40)	1.63 (1.68)
10.	$[RuCl_2(AsPh_3)_2(Morphdtc)]$	63	$C_{41}OH_{38}NS_2As_2Cl_2Ru$	Pale green	135	52.02 (52.29)	4.02 (4.31)	1.48 (1.49)
11.	$[RuBr_2(AsPh_3)_2(Morphdtc)]$	65	$C_{41}OH_{38}NS_2As_2Br_2Ru$	Brown	156	47.55 (47.51)	3.67 (3.77)	1.35 (1.32)
12.	$[RuBr_2(PPh_3)_2(Morphdtc)]$	69	$C_{41}OH_{38}NS_2P_2Br_2Ru$	Brown	150	51.96 (51.73)	4.01 (4.22)	1.48 (1.41)

Table II. IR and Electronic Spectra of Ru(III) Complexes

Sl. No.	Complexes	νC=N (cm^{-1})	ν C=S (cm^{-1})	λ_{max}(ε =M^{-1},cm^{-1}) (nm)
1.	$[RuCl_2(PPh_3)_2(Pipdtc)]$	1470	980	445(1580), 255(2580)
2.	$[RuCl_2(AsPh_3)_2(Pipdtc)]$	1475	995	450(1653), 250(3637)
3.	$[RuBr_2(AsPh_3)_2(Pipdtc)]$	1470	1000	250(3637), 275(3226)
4.	$[RuBr_2(PPh_3)_2(Pipdtc)]$	1460	990	425(1890), 275(3029)
5.	$[RuCl_2(PPh_3)_2(Pzdtc)]$	1460	995	265(3559)
6.	$[RuCl_2(AsPh_3)_2(Pzdtc)]$	1480	1000	465(2505), 280(3073), 250(2695)
7.	$[RuBr_2(AsPh_3)_2(Pzdtc)]$	1480	1000	250(1810)
8.	$[RuBr_2(PPh_3)_2(Pzdtc)]$	1460	995	460(1278), 260(2769)
9.	$[RuCl_2(PPh_3)_2(Morphdtc)]$	1480	1000	440(1958), 265(3875)
10.	$[RuCl_2(AsPh_3)_2(Morphdtc)]$	1480	1000	445(1844), 255(3926)
11.	$[RuBr_2(AsPh_3)_2(Morphdtc)]$	1475	980	450(932), 305(1346), 250(4298)
12.	$[RuBr_2(PPh_3)_2(Morphdtc)]$	1480	995	305(1450), 250(3996)

in the case of monodentate behaviour[15-17]. Further confirmation of such a behaviour of ligands comes from the analysis of the position of the ν C=N mode. In fact this band undergoes a blue-shift in all the complexes, while in the case of unidentate behaviour, this stretching mode would shift towards lower wave numbers or remains unchanged at the same value of the free dithiocarbamate sodium salt.[18]

Electronic Spectra

The electronic spectra of all the complexes in dichloromethane showed two bands in the region 465-250 nm (Table II). The ground state of Ru(III) (t_{2g}^5 configuration) is $^2T_{2g}$ and the first excited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$ which arise from the $t_{2g}^4e_g^1$ configuration.[19] In most of the ruthenium(III) complexes the UV and visible spectra show only charge transfer bands.[20] Based on the values of the extinction coefficient, all bands have been assigned to charge transfer transitions arising from an excitation of an electron from the metal t_{2g} level to unfilled molecular orbitals derived from the π^* level of the ligands. There is another possibility that the absorption behaviour could involve ligand to metal charge transfer from the halide ligands. However, the nature of the spectra and the extinction coefficients show a similarity to the spectra of other octahedral Ru(III) complexes[21-23] wherein a metal to ligand charge transfer has been indicated. Hence, we propose a metal to ligand charge transfer transitions for all the Ru(III) complexes.

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12.	$[RuBr_2(PPh_3)_2(Morphdtc)]$	1480	995	305(1450), 250(3996)

Table III. EPR Spectral Data for Ru(III) Complexes

Sl.No.	Complex	g_1	g_2	g_3	$\langle g \rangle^*$
1.	$[RuCl_2(PPh_3)_2(Pipdtc)]$	2.25	2.25	2.11	2.20
2.	$[RuCl_2(AsPh_3)_2(Pipdtc)]$	-	2.18	-	-
3.	$[RuCl_2(PPh_3)_2(Zzdtc)]$	2.21	2.21	2.16	2.19
4.	$[RuCl_2(AsPh_3)_2(Pzdtc)]$	-	2.19	-	-
5.	$[RuBr_2(AsPh_3)_2(Pzdtc)]$	2.23	2.23	2.15	2.20
6.	$[RuCl_2(AsPh_3)_2(Morphdtc)]$	2.22	2.22	2.15	2.20
7.	$[RuBr_2(AsPh_3)_2(Morphdtc)]$	-	2.21	-	-

$$\langle g \rangle^* = \left(\frac{1}{3} g_1^2 + \frac{1}{3} g_2^2 + \frac{1}{3} g_3^2\right)^{1/2}$$

-0.28V (reduction) vs an Ag/AgCl electrode (Table IV). The redox processes observed for these complexes are only metal centered Ru^{IV}-Ru^{III} and Ru^{III}-Ru^{II} couples. Some of the complexes showed reversible redox couples with peak-to-peak separation (Δ Ep) values ranging from 60-70 mV which is characteristic of a single step one electron-transfer process[26-28]. The triphenylphosphine complexes of the type $[RuCl_2(PPh_3)_2(Pzdtc)]$ showed an irreversible oxidation at 0.69 V and a reversible reduction at -0.19 V. The complexes $[RuCl_2(PPh_3)_2(Pipdtc)]$ and $[RuBr_2(AsPh_3)_2(Morphdtc)]$ showed only irreversible oxidations and reductions. The reason for the irreversibility for these complexes may be due to a short-lived oxidised and reduced state of the metal ion.[29] Hence, from the electrochemical data it is inferred that the present ligand system is ideally suited for stabilizing the higher oxidation states of ruthenium ion.

Antifungal Activity

Pipdtc, Pzdtc, Morphdtc and their ruthenium(III) complexes show a fair degree of activity against the fungus Fusarium sp. However, the ligands show a poorer inhibitory effect than their complexes. The toxicity increases with increasing the concentration of the complexes (Table V). The antifungal activity of the complexes with respect to the ligands in general vary in the order Pzdtc > Pipdtc > Morphdtc. The reason for the fungicidal activity of the compounds may be due to the presence of the C=S group present in the ligands as well as in their complexes.[30]

Table IV. Cyclic Voltammetric Data of Some Ru(III) Complexes

Sl. No.	Complex	Ru^{IV}-Ru^{III} couple Ef(V)	Ru^{IV}-Ru^{III} couple ΔEp(mV)	Ru^{III}-Ru^{II} couple Ef(V)	Ru^{III}-Ru^{II} couple ΔEp(mV)
1.	$[RuCl_2(PPh_3)_2(Pipdtc)]$	0.75	-	-0.16	-
2.	$[RuCl_2(AsPh_3)_2(Pipdtc)]$	0.62	60	-0.16	70
3.	$[RuCl_2(PPh_3)_2(Pzdtc)]$	0.69	-	-0.19	60
4.	$[RuCl_2(AsPh_3)_2(Pzdtc)]$	0.64	60	-0.28	60
5.	$[RuBr_2(PPh_3)_2(Pzdtc)]$	0.61	65	-0.18	70
6.	$[RuCl_2(AsPh_3)_2(Morphdtc)]$	0.75	70	-0.16	60
7.	$[RuBr_2(AsPh_3)_2(Morphdtc)]$	0.75	-	-0.25	-

* Supporting electrolyte : $[NEt_4]ClO_4$ 0.05M; Ef = 0.5 (Epa + Epc), where Epa and Epc are anodic and cathodic peak potentials, respectively; scan rate 50 mVs^{-1}; all potentials are referenced to Ag/AgCl.

Table V. Antifungal Activity of Ru(III) Complexes

Sl. No.	Compound	% Inhibition Fusarium sp ($\mu g\ L^{-1}$) 100	200	300	400	500
1.	Pipdtc	7	10	12	15	17
2.	$[RuCl_2(PPh_3)_2(Pipdtc)]$	10	12	20	30	40
3.	Pzdtc	6	11	14	15	19
3.	$[RuCl_2(PPh_3)_2(Pzdtc)]$	12	18	25	32	42
4.	Morphdtc	6	8	12	13	15
5.	$[RuCl_2(PPh_3)(Morphdtc)]$	9	14	19	28	36

The IR spectra of the complexes clearly indicate the chelated nature of the dithiocarbamate showing the coordination through the two sulphur donor atoms. The electronic spectral data indicate an octahedral geometry for the complexes and they are very similar to other Ru(III) complexes reported earlier.[21-23] From the EPR data (discussed earlier), It has been suggested that there is some kind of distortion from perfect octahedral geometry for some of the complexes based on the number of lines observed in the EPR spectra. The cyclic voltammetric studies show a single step one electron transfer processes which are metal centered in all the complexes and there is no marked influence on the electron transfer processes from the presence of different types of ligands in the complexes. On the basis of the elemental analyses, IR, electronic spectra, EPR spectral data and cyclic voltammetric data the octahedral structure in Fig. 2 has been tentatively proposed.

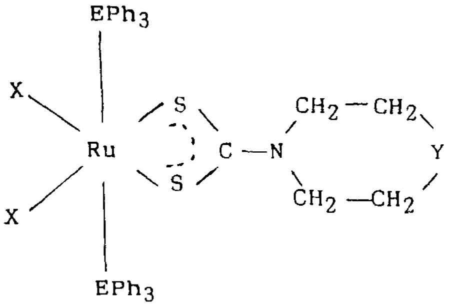

Fig. 2. Suggested Structure of the Ruthenium Complexes

(X = Cl or Br; E = P or As; Y = O, Morphdtc

= CH_2, Pipdtc

= NH, Pzdtc

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