Electrical Conductivity, Electronic Absorption, IR and NMR Studies On Cr(III), Sn(IV) and Pb(IV) Complexes of an Azo Ligand derived from Isatin and 4-Aminoantipyrine.

Chinyere E. E*., Ukoha P. O., Agbo J. N and Obasi L. N
Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Enugu State, Nigeria
E-mail: chinyereevans@yahoo.com: +2348030999585

ABSTRACT

The electrical conductivity, electronic absorption, IR and NMR spectroscopy of an azo ligand synthesized by coupling IH-indole-2,3-dione(isatin) with diazotized I-phenyl-2,3-dimethyl-4-aminopyrazole-5-one (4-aminoantipyrine) have been studied. The ligand: 6-[(E)-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-lH-pyrazole-4-yl)diazenyl]-lH-indole-2,3-dione(DPDD), forms stable complexes with metal ions, such as Cr(III), Sn(IV) and Pb(IV). These complexes have potential application in pharmacology. Their structures were investigated by UV and IR spectroscopy. Analytical data on the composition of the complexes show that Cr(IV) and Sn(IV) formed complexes with 2:l metal-ligand mole ratio, whereas complexation with Pb(IV) followed 2:1 metal-ligand stoichiometry.

Keywords: Azoligand; DPDD; metal complexes; 4-aminoantipyrine; isatin; Cr(III); Sn (IV); Pb(IV).

INTRODUCTION

Antipyrine (2,3-dimethyl-1-phenyl-5-pyrazolone) was first synthesized by knorr in 1883. Since the synthesis, a lot of interest has been paid to this group of compounds due to their properties, which prompted the search for other pyrazolones with similar behaviour but with enhanced activities[1]. 4-aminoantipyrine is an amino-derivative of antipyrine. Among the pyrazolone derivatives, 4-aminoantipyrine forms a variety of compounds with ketones (such as isatin), and they are reported to be superior reagents in biological, pharmacological, clinical and analytical applications [2].

Isatin (IH-indole-2,3-dione) is an indole denvative [3-15]. The compound was first obtained by Erdman and Laurent in 1841, as a product from the oxidation of indigo dye by nitric and chromic acids[13-15]. Isatin has a synthetic versatility which has led to its extensive use in organic synthesis. The N-substituted isatin has been frequently used as intermediates and synthetic precursors for the preparation of a wide variety of heterocyclic compounds used as raw materials for many drugs and reagents for metal ion studies [12, 16].

The synthesis of a heterocyclic product from 4-aminoantipyrine and isatin requires coupling. Ordinarily, amines do not couple; the coupling however is preceded by diazotization, which introduces an azo functional group to the 4-aminoantipyrine ring to aid a linkage with Isatin. Many synthetic pathways have been employed in obtaining azo ligands derived from 4-aminoantipyrine and ketones; these derivatives have been established to form compounds with several elements in the periodic system [1, 17,18]. The method of Heinosuke Yasuda has been used in the synthesis of azoligand and its (Co (II), Fe(III) and OS(VIII) complexes. The complexes were obtained following the method of El Saied *et l* [19-21].

In the present work, an azobase ligand; 6-[(*E*)-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)diazenyl]-1*H*-indole-2,3-dione, herein referred to as DPDD, has been synthesized from 4-aminoantipyrine and isatin in the same way that it had been synthesized[19-22]. This work has been prompted by the need to make further studies on the complexing and ion-discriminating ability of the ligand. Attempts to obtain Cd(II), Sn(II) and Pb(II) complexes of DPDD proved abortive. However Cr(III), Sn(IV) and PB(IV) complexes have been obtained. This paper therefore reports the electrical conductivity, spectroscopic characterization, as well as the proposed structures of these complexes synthesized with DPDD.

MATERIALS AND METHODS

Apparatus and reagents

Reagent grade chemicals were used without further purification. IR spectra were recorded with Schimadzu Infrared Spectrophotometer. The electronic spectra were carried out in ethanol solution using a Jenway 6305 UV/Visible Spectrophotometer. The ^{I}H and ^{13}C NMR spectra were recorded in DMSO using 200 MHz Varian Nuclear Magnetic Resonance Spectrophotometer. Molar conductivity of the ligand and complexes were measured in de-ionized water, using a Siemmen (WTW) Conductivity Meter-LF 90 series.

Synthesis of DPDD

DPDD was synthesized according to reported methods[19, 20 ,22]. 0.1218 g of 4-aminoantipyrine (0.0006 M) was dissolved in 1.0 cm^3 of conc. HCl (37 %) in 5.0 cm^3 of distilled water, and was diazotized with $NaNO_3$ solution (0.06 g) in 2.0 cm^3 of distilled water below 5.0 ^{o}C, with hand stirring. The resulting diazotized 4-aminoantipyrine was immediately poured into a mixture of 0.0882 g of isatin (0.0006 M) and 2.5 g of sodium acetate (0.0305 M) in 30 cm^3 distilled water, using mechanical stirring at ice temperature. After 45 minutes, a coloured product was formed, which was collected, washed with cold ethanol (96 %) in water. The product was recrystallized from ethanol and water.

Synthesis of the complexes

Cr(III), Pb(IV) and Sn(IV) Complexes of DPDD were synthesized according to literature [21]. 20 cm^3 of hot ethanolic solution of the corresponding metal salt which contained 0.0006 M concentration of each metal ion was reacted with hot ethanolic solution of the ligand (0.0003 M) and refluxed for 3-4 hours at 60 ^{o}C. On cooling, the coloured product separated out in each case. It was filtered and washed with cold ethanol (90 %) and dried under vacuum over $CaCl_2$.

RESULTS AND DISCUSSION

Spectral studies of the ligand and its complexes

Electronic spectra

Table 1.0: Electronic Spectral Data 0f the Ligand and its Complexes

Compound	Wavelength (nm)	Absorbance	Molar Absorptivity ($Lmol^{-1}cm^{-1}$)
Ligand	209.0	2.232	3100.00
	241.0	3.000	4166.67
	296.2	0.517	718.06
	419.8	0.145	201.39
Cr(III) Complex	208.6	1.539	2137.50
	242.0	2.337	3245.83
	298.8	0.423	587.50
	361.0	0.077	106.94
	446.4	0.090	125.00
	517.2	0.028	38.89
Sn(IV) Complex	211.4	1.838	2552.78
	242.2	2.873	3990.28
	297.6	0.509	706.94
	421.4	0.110	152.78
Pb(IV) Complex	201.8	0.462	641.67
	226.4	0.125	173.61
	299.6	0.028	38.89
	360.0	0.042	58.33
	417.4	0.019	26.39
	498.0	0.019	26.39
	657.2	0.015	20.83

The electronic spectral data of the ligand and its Cr(III), Sn(IV) and Pb(IV) complexes are found in Table 1.0. As reported in the literature [23-25], the electronic spectrum of the ligand shows four main absorptions in ethanol, between 209.0-419.8 nm, as seen in the Table 1.0. The fist (209.0 nm) and second (241.0-296.2 nm) are assigned to π-π* transition of the conjugation of the aromatic ring. The band at longer wavelength (419.8 nm) can be assigned to an intramolecular charge transfer, originating from the 4-aminoantipyrine ring to the C=0 as a sink; this is also the case with 360 and 361 nm observed in Cr(III) and Pb(IV) complexes respectively. All the absorptions around 209 and 296.2 nm in the complexes are ascribed to intra ligand transitions.

The complexes show bathochromic (red) shift, due to increased stability of the complexes, lowering their energies and the energy of the transition of the excited states. Cr(III) shows maximum absorption at 446.4 nm; Sn(IV) complex at 424.4 nm and Pb(IV) complex at 498.0 nm. Both metal to ligand charge transfer (MLCT) and d-d transition respectively were absent in Cr(III), Sn(IV) and Pb(IV) complexes. The UV spectra of the ligand and complexes are shown in Figures 1,2,3 and 4.

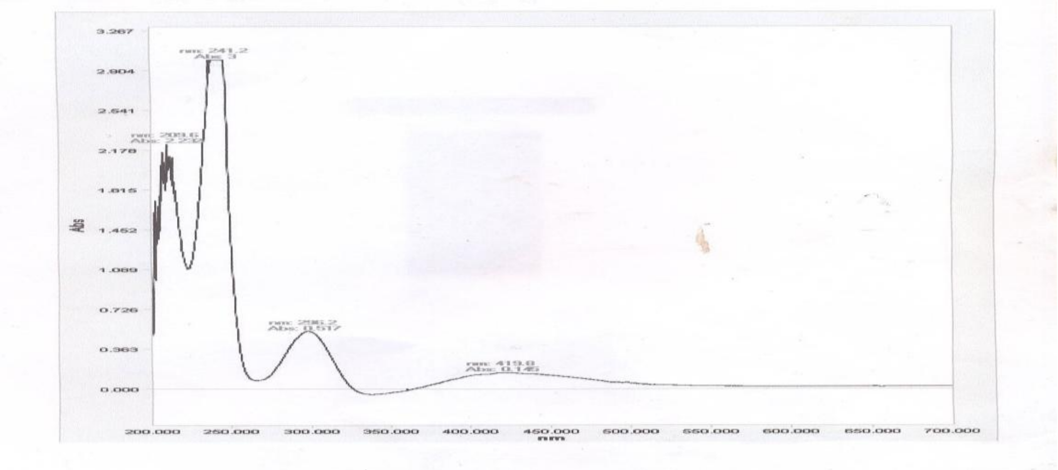


Figure: 1 The UV Spectrum of the Ligand

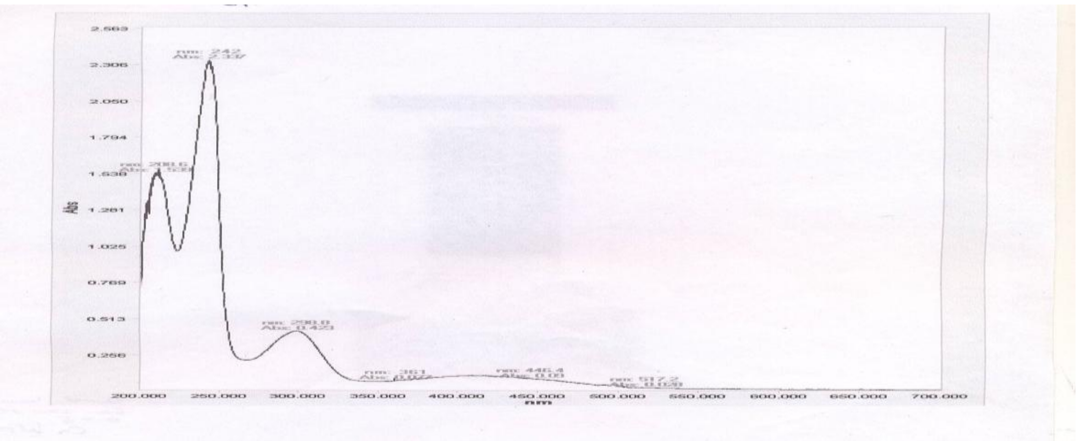


Figure:2 The UV Spectrum of Cr(III) Complex

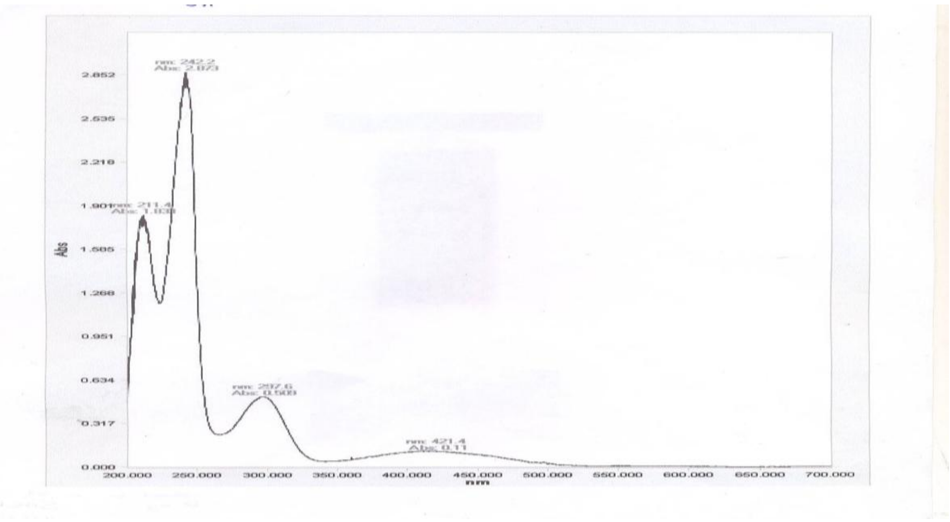


Figure: 3.The UV Spectrum of Sn(IV) Complex

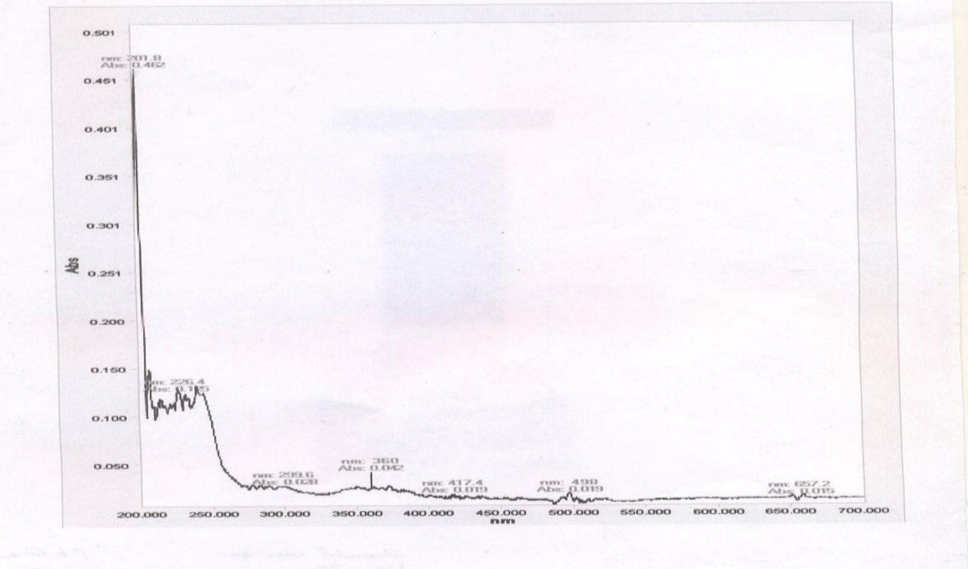


Figure: 4.The UV Spectrum of Pb(IV) Complex

Infrared spectra

Table 2.0: Infrared Spectral Data of the Ligand and its Complexes

Ligand	**Cr(III) Complex**	**Sn(IV) Complex**	**Pb(IV) Complex**	**Assignments**
3447.87 m	3446.91 w	3453.66 m	3713.09 w 3655.23 w 3512.49 w	v(N-H) of isatin ring
3213.51 w	3221.23 w	-	3363.66 w 3263.66 w	v(O-H) (hydrogen bonded) as a result of lattice water
2897.18 m	2900.07 w	2901.04 m	-	v(C-CH_3)
2819.06 m	2820.02 w	2820.99 m	2797.84 w	v(N-CH_3)
1740.81 w	1740.81 w	1736.89 w	1752.39 w	v(C=O)
1609.65 w	1607.72 w	1612.54 w	1606.76 w	v(N=N)
1464.02 w 1399.40 w	1400.37 w 1462.09 w	1407.12 s 1465.95 w	1450.52 w	v(C=C) of aromatic
1320.00 w 1277.88 w 1201.69 w	1317.43 w 1200.73 w	1332.86 m 1278.85 m 1201.69 m	1323.21 w 1193.01 w	v(C-N) and v(C-H) merging vibrations of the pyrazolone ring
1095.60 m	1094.64 w	1096.57 s	1058.96 w	v(N-N)
-	751.30 w 659.68 w	757.09 s 711.09 s	682.82 w 756.12 w	M-O bond stretching
-	561.30 s 466.78 s	469.68 s	-	M-N bond stretching
-	393.49 s 385.78 s	397.35 s	389.63 m	M-Cl bond stretching

Legend: m = medium; w = weak; b = broad; s = strong; sh = sharp

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation, all data are listed in Table 2. The IR values include intensities for the amine, azo and carbonyl bands in addition to other additional bands in isatin, pyrazolone and the complexes respectively. The results are compared with those previously reported for 4-aminoantipyrine based ligands and are discussed in terms of relative importance.

The band at 3447.87 cm^{-1} is characteristic of both phenol and amine groups [26] but is however ascribed to the amine group of the isatin ring [27]. The IR spectra of the complexes show general broadening of v(N-H) bands. This group shifted to 3446.91, 3453.66 cm^{-1} in Cr(III) and Sn(IV) complexes respectively. In Pb(IV) complex, v(N-H) appeared at 3713.09, 3655.23 and 3512.49 cm^{-1} respectively; they all indicate the involvement of the amine nitrogen in coordination.

Peak for v(O-H) group in the free ligand was observed at 3213.51 cm^{-1}. It shifted to 3221.23 cm^{-1} in the Cr(III) complex, but was not found in the Sn(IV) complex. v(O-H) band appeared at 3263.66 cm^{-1} in the Pb(IV) complex. The OH group in the ligand and the complex could be due to the presence of lattice water.

The assignment of C=O bands agrees with the literature [19.] The C=O stretching frequency of the ligand appeared at 1740.81 cm^{-1}. It did not change in Cr(III)-DPDD complex but shifted to 1736.89 and 1752.39 cm^{-1} in Sn(IV) and Pb(IV) complexes respectively. 1609.65 cm^{-1} found in the ligand was due to the v(N=N). This band; v(N=N) was seen at 1609.72, 1612.54 and 1606.76 in the Cr(III), Sn(IV) and Pb(IV) complexes respectively. They are weak bands due to the non-polar nature of the bond. They reveal conjugation, and participation of azo nitrogens in coordination with the metal ions [19].

Vibrational frequencies of v(N-CH_3) occurred at 2819.06 cm^{-1} in the ligand. It was slightly increased to 2820.99 and 2820.02 cm^{-1} in Cr(III) and Sn(IV) complexes, suggesting the participation of the azomethine nitrogen in coordination with Cr(III) and Sn(IV) respectively. This band was lowered to 2797.84 cm^{-1} in Pb(IV) complex.

The appearance and changes of v(N-H) of isatin, v(N-CH_3), v(N=N) and v(C=O) in both the ligand and the complexes are evident of their participation in coordination.

Nuclear Magnetic Resonance Spectral Studies

The NMR spectral studies were limited to that of the free ligand [22], it was suspected that the spectra of the Cr(III), Sn(IV) and Pb(IV) complexes would be dominated only by the DPDD bands. The NMR data are given in Table 3 and 4 respectively. The data for IHNMR and ^{13}CNMR are given here as it has been obtained for this particular ligand [16,19,22].

Table 3: ^{I}HNMR Spectral Data of DPDD in $CDCl_3$ relative to TMS (ppm)

Peak (δ)	Assignment
2.45 (3H,s)	C–CH_3 methyl protons from pyrazolone ring
3.40 (3H,s)	N–CH_3 methyl protons from pyrazolone ring
6.89-7.59 (8H,m)	Phenyl protons
11.04(1H,s)	N-H proton of isatin ring

Legend: H = Hydrogen; s = singlet; d = dublet; m = multiplet

The spectrum of DPDD displays a signal for C-CH_3 as a singlet at 2.45 δ, which is due to the three chemically equivalent protons of the substituted aliphatic methyl group on the pyrazolone ring of DPDD. The signal for N-CH_3 appeared as a singlet at 3.40 δ. This signal is a sharp peak indicative of hydrogen bonding, and occurs as a result of shielding of the three chemically equivalent protons on the nitrogen of the pyrazolone ring.

The characteristics of aromatic protons include their ability to display low field absorptions at 6.5 – 8.0 δ. There are three sets of chemically equivalent protons of the aromatic (phenyl) ring in the structure. The signals for these phenyl protons appeared as multiplets at 6.858 – 7.593 δ with powerful deshielding due to the circulating electrons in the field. It was expected that the signal for the phenyl protons would display a singlet for five protons as generalized for monosubstituted benzenes; rather, a multiplet similar with the results on other pyrazolones was borne out in practice.

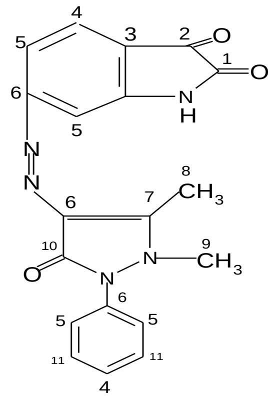
Signal for the NH proton of isation (an indole) appeared as a singlet at 11.04 δ. This proton is on a heteroatom, and can undergo partial or complete decoupling by electrical quadrupole effects of some heteroatoms. The peak is sharp, and is evident of the absence of protons on the adjacent carbons to which coupling could take place. If protons are present on the adjacent carbons to NH, they can be split by the NH to give a broad peak. However, this was not observed and hence the assignment of 1H,s at 11.04 δ to the NH of isatin. This further reveals that NH did not suffer any coupling effect, but was rather deshielded with a down field shift. There is no significant difference with the peaks obtained so far for C-CH_3, N-C_6H_5, NH and other phenyl protons with what have been obtained so far in compounds where they are present [19,22,23,26,28].

The ^{13}CNMR results obtained for DPDD are complementary to that of its ^{I}HNMR results, and the assignments agree with reports on pyrazolones[19, 22]. These carbons possess non-equivalent nuclei like the protons and appeared at different applied field strengths.

Signals for the Sp^3-hybridized methyl carbons are found up field between 39.34-40.98 ppm. Signals for the Sp^2-hybridized carbons of the aromatic (benzene) ring are displayed at 112.88-139.05 ppm. These aromatic carbons are highly deshielded as in ^{I}HNMR and fall in far down field of the methyl carbons.

Signal for ethylene carbons in the structure appeared at 151.38 ppm. The signal at 160.04 ppm is assigned to the carbonyl carbons in the structure. The number of signals displayed in the ^{13}CNMR spectrum is not up to what is expected in the structure. Unlike in ^{I}HNMR spectrum, the greater range of relaxation times in carbons limits the number of carbons giving rise to the signals.

Table 4: ^{13}CNMR Spectral Data of the Ligand

	^{13}C (ppm)	Structure showing carbon numbering
C_1	160.011	
C_2	139.051	
C_3	40.975	
C_4	112.884	
C_5	40.971	
C_6	125.364	
C_7	123.445	
C_8	39.336	
C_9	40.581	
C_{10}	151.379	
C_{11}	118.475	

Conductivity Measurements and Physical Characteristics of DPDD and the Complexes

Table 5: Physical Data of the DPDD and its Cr (III), Sn (IV) and Pb (IV) Complexes

Compound	**Colour**	**Texture**	**Melting Point(0^{o}C)**	**Yield (g)**	**% Yield**	**Molar Conductivity (μScm^{-1})**
Ligand	Red	Crystalline	184-185	1.805	34.38	66.90
Cr(III) Complex	Pale-Red	Crystalline	178-179	0.325	95.59	9.90
Sn(IV) Comple	Orange-Red	Crystalline	186-188	0.245	74.24	9.70
Pb (IV) Comple	Brown	Powdery	248-250	0.225	70.31	89.90
KCl Salt	-	-	-	-	-	370.00
$CuSO_4.5H_2O$	-	-	-	-	-	570.00

Table 5 shows the molar conductivity values of 10^{-3} M aqueous solutions of the ligand (DPDD), the complexes and some metal salts respectively at room temperature (25 ^{o}C). Cr(III) and Sn(IV) complexes have very low values, suggesting the distribution of the anions within the nuclear axis without any appreciable dissociation. As a result, the Cr(III) and Sn(IV) complexes possess extra stability than DPDD and are non-electrolytes. The ligand (DPDD) and Pb(IV) complex show higher values, at 66.90 and 89.90 μScm^{-1} respectively, which suggest electrolytes behavior [29,30]. The values of the ligand and its complexes were very low with respect to the values of KCl and $CuSO_4.5H_2O$ used as control.

Composition of the complexes and proposed structures

The stoichiometric studies of the complexes were determined by employing slope-ratio method. The analytical data obtained revealed that Cr(III) and Sn(IV) formed complexes, with 2:1 metal-ligand stoichiometry, whereas Pb(IV) gave a complex with 1:1 metal-ligand mole-ratio when reacted with the ligand respectively [31].

Structures have been suggested based on the various spectra data obtained. The proposed structures for the ligand and the complexes are given in Figures 5,6,7 and 8. The Cr(III) and Sn(IV) complexes respectively are all octahedral structures. One of the azo nitrogen is attached to a metal ion, with the anions coordinating within the nuclear axis. This arrangement reduces the easy flow of electrons and therefore position the metal centers for cooperative reactivity to ensure stability of the resulting complexes [32]. The appearance of NH band in the structures of Cr(III) and Pb(IV) complexes respectively is as a result of coordination without deprotonation of the isatin nitrogen. The Pb(IV) complex has an octahedral structure.

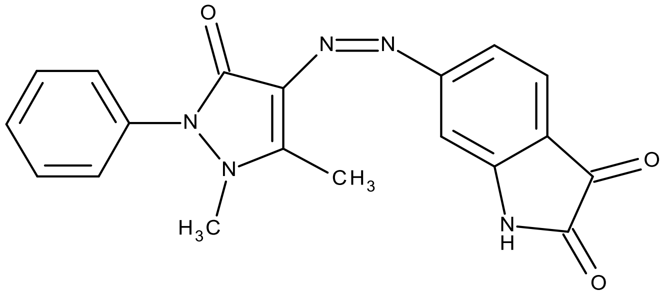
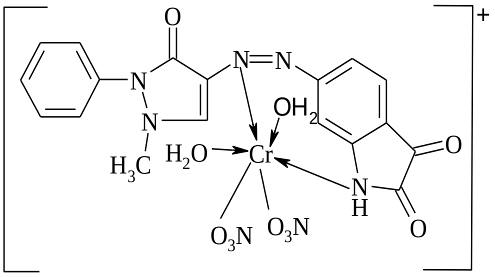
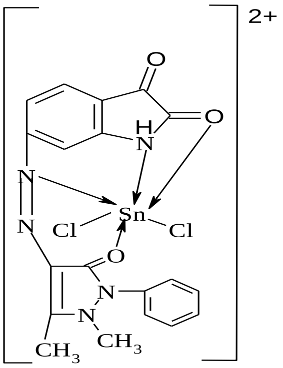


Fig: 5. The Ligand

6-[(*E*)-(1,5-dimethyl-3-oxo-2-phenyl-2,3- dihydro-1*H*- pyrazol-4-yl)diazenyl]-1*H*-indole-2,3-dione.





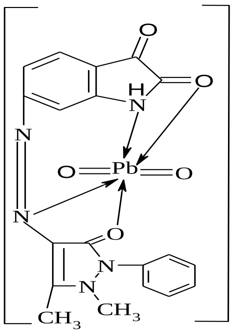


Fig: 6. chromium (III) Complex

Fig: 7. tin(IV) Complex

Fig: 8. lead (IV) Complex

CONCLUSION

The metal complexes of an azo ligand synthesized by coupling I*H*-indole-2,3-dione with diazotized l-phenyl-2,3-dimethyl-4-aminopyrazole-5-one, have been studied. The structures for these complexes are octahedral and have been proposed based on the various spectra data obtained for Cr(III), Sn(IV) and Pb(IV) respectively. This research gives an insight over the potential of DPDD in the spectrophotometric determination of metal ions such as Cr(III), Sn(IV), Pb(III) etc.

ACKNOWLEDGEMENT

Thanks are due to the Joint Development Authority of Nigeria and Sao-Tome & Principe, Petroleum Technology Development Fund of Nigeria and Department of Pure & Industrial Chemistry, University of Nigeria, Nsukka for supporting the research on 4-aminoantipyrine base ligands and metal complexes.

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