Biohouse, Volume 1: Issue 3, Sept-Oct 2015

Biohouse Journal of Research in Science

ISSN 2379-1527

Ruthenium Spectroscopic Analysis of Thiocorbomate Metal Complex

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Abstract: *Ruthenium(III) complexes of dithocarbomate ligand have been prepared in situ by condensing of a substituted 2 hydroxy 3-methyle pyramidine compound with corbondisulphide . These were characterized by elemental analysis, m.p., IR, molar conductivity, magnetic moment measurements, and electronic spectra. The free ligands were also characterized by 1H NMR spectra. The thermogravitic analysis discussed in terms of possible groups effects. The electronic spectra of the free ligand and the complexes are compared and discussed. The electrospray ionization (ESI) mass spect ra of four free ligands and their complexes were measured. Infra red spectra and The deconvolution of the visible spectra of the complexes, and are assigned to the three d–d transitions , 4B1g → 4Eg (4T2g); 4B1g → 4B2g(4T2g); 4B1g → 4Eg(4T1g), respectively. The complexes showed magnetic moment in the range of 3.5–4.2 BM which corresponds to three unpaired electrons.*

Key Words: Ruthenium, Electranic spectra, ir, nmr,mass, uv, Mass visible spectra

I. INTRODUCTION

Main group dithiocarbamate complexes find wide-ranging applications in materials and separation science, and have potential use as chemotherapeutics, pesticides, and fungicides. The literature on main group dithiocarbamates as a whole has not been reviewed extensively since the 1970s (1, 2) despite the large number of publications that have appeared subsequently. From an inorganic chemistry stand point, dithiocarbamates are highly versatile ligands toward main group metals. They can stabilize a variety of oxidation states and coordination geometries, and seemingly small modifications to the ligand can lead to significant changes in the structure–behavior of the complexes formed. This chapter focuses primarily on structural aspect of main group dithiocarbamate complexes, covering the essential literature from 1978 to 2003. For the purposes of this chapter, the zinc triad of elements is not considered as being main group: Zinc dithiocarbamate complexes of this volume on transition metal dithiocarbamates by Hogarth. The structural parameters of the dithiocarbamate ligands themselves are not modified significantly on coordination to main group elements. Distances (A °) and angles (_) are in the range: C__N(R2) ¼ 1.24–1.52 (1.33 mean); C__S ¼ 1.52–1.82 (1.72 mean); SCS ¼ 110.1–128.9 (118.6 mean). The two C__S distances are often slightly different, indicating some charge localization: as one would expect, the shorter C__S are generally associated with the S atom that is least strongly associated with the metal center. The SCS bond angle generally increases in line with the size of the metal to which the dithiocarbamate is coordinated. Extensive use has also been made of infrared (IR) spectroscopy for the characterization of dithiocarbamate complexes. Particular diagnostic use has been made of the C__N(R2) and C____S stretching modes, which fall typically in the range 1500 _ 50 and 980 _ 50 cm_1, respectively. polymers in the solid state., with the stereochemically active lone-pair equatorial [Fig. 35(a)]. The dithiocarbamate ligands are anisobidentate; the asymmetry decreases essentially in line with increasing electronegativity of the metal atom substituents (i.e., with increasing Lewis acidity of the metal center). For dialkyl complexes the M__S distances are in the range 2.43–2.55A ° (short) and 3.10–3.30A ° (long); the normalized Pauling bond order (360) of the latter is _0.22 (av). The M__S lengths are considerably longer in the\ triorganyl complexes [_3.10 (short) and 3.60A ° (long)] (368, 369), indicating a very weak interaction between the dithiocarbamate and the metal moiety. As would be expected, the M__S bonds are much shorter (2.43 and 2.68A °) in the
. The NMR spectra of the mono(dithiocarbamate) complexes are generally difficult to interpret due to ligand exchange reactions, metal-centered rearrangements and reductive elimination reactions occurring quite rapidly on the NMR time scale (358–360): The occurrence of these processes indicates that the dithiocarbamate is only weakly bound to Te. Furthermore, conductimetry measurements show the triphenyl complexes [are close to 1:1 electrolytes, again indicative of the dithiocarbamate.

II. MATERIALS AND METHODS

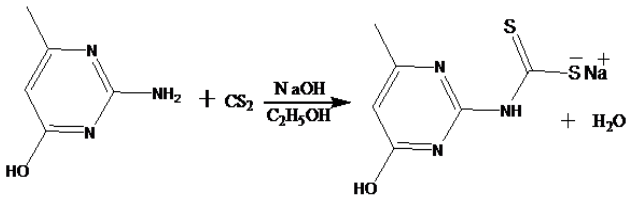
Ruthenium chloride anhydrous was obtained from Fluka,2-Amino, 3-methyl 4-Hydroxy pyramidine and carbon disulfide werepurchased from Aldrich. Other chemicals used were of analytical reagent or higher purity grade. Solvents used were of reagent grade and purified before use by the standard methods. Conductivity measurement was carried out by a Systronics condu ctivity bridge 305, using a conductivity cell of cell constant 1.0 doubly distilled water was used as solvent. Electronic absorption spectra on JAS.CO UV/VIS-7850 recording spectrophotometer. Infrared spectra was recorded on a JAS.Co-460 plus FT-IR spectrophotometer in the range of 4000-400 cm-1 in KBr pellets. Micro chemical analysis of

carbon, hydrogen and nitrogen for the complexes were carried out on a Herause CHNO-Rapid elemental analyzer.1H NMR spectra were recorded on a Brucker DRX-500 Advance spec trome ter at 500MHz in DMSO-discussing tetramethylsillane as internal reference standard. Melting points were measured on a unimeltcapillary melting Point apparatus and reported uncorrected

Synthesis of Sodium salts of dithiocarbamate ligands

2–amino-4-hydroxy-6-methylpyrimidine (AHMPDTC)

0.1 mol of amine was dissolved in 50 ml of Absolute ethyl alcohol in a clean beaker which was placed in ice. To this cold solution add 10 ml of Sodium hydroxide (10N) solution, and then add Pure Carbon disulphide (, 0.1 mol) in drop wise through separating funnel in about 30 min with constant stirring. The contents were stirred mechanically for about 30 min, sodium salt of dithiocarbamate precipitated out. It was dried and recrystallised from methanol and dried in vacum over calcium chloride. Synthetic procedures yield and melting points were mentioned below.



Metal salts used for the Dithiocarbamate complexes

Ruthenium TriChloride	$RuCl_3$ $3H_2O$	261.47	SRL CHEMICALS

Preparation of Dithiocarbamate Metal complexes

The aqueous solution of 0.1 mol of metal salts was added with constant stirring to an aqueous solution of 0.1mol of Sodium dithiocarbamate ligand. The reaction mixture was stirred at room temperature for 2 hours. The colored precipitates were obtained. The precipitates were filtered and washed with water and then with Methanol and dried over calcium chloride in a desiccator. All the complexes were prepared in 1:2 ratios of Metal to Ligand.

III. Results and Discussions

Infrared spectral ananlysis of 2-amino 3-hydroxy 6-methyle pyramidine dithiocarbamate ligand:

The typical I.R spectrum of AHMPYDTC dithiocarbamate was presented in the Fig As concern the 2-Amino 4-hydroxy-6-methyl pyridine dithiocarbamate , two main regions of the I.R. are of main interest the most significant bands recorded in the FT-IR spectra of the ligand and its metal complexes are reported in the Table 2.4.1

First, the (1450-1550 cm-1) region, which was primarily associated with υ (N-CSS) stretching vibrations. Second, the 950-1000 cm-1 region, which is associated with υ (C-S) stretching vibrations.[3]

The characteristic band at 1443.01cm-1, was assignable to υ (N-CSS); this band defines a carbon Nitrogen bond order between a single bond (υ =1250-1350cm-1) and a double bond (υ = 1640–1690cm-1). The appearance of a band in that region 1641 cm-1 indicates that, of the three possible resonance structures reported by Chart et al., characterized by a strong delocalization of electrons in the dithiocarbamate moiety.

A single sharp band at 1004.01 cm-1 was assigned to the stretching vibrations of the C-S bond. The band at 3404.32 cm-1 associated with the υ(N-H) stretching and OH stretching vibrations. Sharp band absorved in the region of -2979.08 cm-1 indicate aromatic =C-H Stretching vibration. The characteristic absorption band at 1523-1620.95 cm^{-1} indicate aromatic C=C stretching vibration of pyridine ring . The absorption bands in appear in between the region of 1115.38–864.21 cm–1 (C–C ,C–O, C–N).

Infrared spectral ananlysis of 2-amino 3-hydroxy 6-methyle pyramidine dithiocarbamate $(AHMPYDTC)_2Ru$ Metal Complexe:

The interpretation of IR spectra of dithiocarbmates comples of Transition metals had arise and considerable interest both diagnostically to determine the mode of co-ordination and as a mean of assessing the nature of bonding in these complexes. The Infrared spectrum of Ru (III) complexes was compared the [AHMPYDTC] lignad. The typical IR Spectrum of [AHMPYDTC] complexes.

A strong band exhibited at 1443.01 cm-1 in the I.R spectrum of the ligand, which was assigned to the Thioureide bond, was shifted to 1443.01-1456.52 cm-1 region. On Passage from the free dithiocarbamate ligand to their complex, the υ(N–CSS) mode is shifted to higher energies, showing an increase of Carbon-Nitrogen double bond character and hence a greater contribution of the structure . The Infrared active υ (N–CSS) mode was sensitive to both chain length and the steric bulk of the substituents. As double character was more pronounced in the complex it can be concluded that the ligand was co-ordinated through S, S atoms.

To discern the bonding type of the dithiocarbamate ligand in their complexes, the Bonati-Ugo method is, by far, the most popular one. It consists of tracing the 940-1060 cm-1 spectral region, where the υ (C-S) modes were thought to appear. In fact, the bands due to CSS moiety was usually coupled to other vibrations and are very sensitive to the environment around this group, but they were also useful to distinguish between Monodentate and Bidentate Co-ordination. The presence of only one band in the investigated region, commonly attributed to υ (SCS) mode, it indicates completely symmetrical bonding of the dithiocarbamate ligand to metal in bidentate mode where as a doublet was expected for the Monodendate coordination.

ISSN 2379-1527

Basing on the above concept the presence of single band at 993.22 cm-1 region was assumed to υ (C-S) stretching vibrational mode and it indicates the symmetric bidentate behavior of the ligand that means the AHMPDTC ligand was co-ordinated through both the sulphur atoms.

Along with these bands new bands were formed which are not observed in the spectrum of the ligand, the band in the resin 597-551 cm-1 was assigned to the υ (M-S) metal ligand bond of the complex. The appearance of broad band at 3458 cm-1 can be assigned to the stretching vibrations of υ- NH and co-ordinated water molecules present in their complexes. In the spectra of both ligand and complex, significant change were observed, for molecular vibrational stretching mode. The two weaker bands at 993-865 cm-1 were assigned respectively to – OH rocking and wagging vibrations of co-ordinated water in the complex.

Compound name	Thiouroid bond	-NH-	C=C-H
AHMPYDTC	1443	3404.02	2979
AHMPYDTC-Ru	1456	3458	2987

-C=C-	C-S	M-S	OH-(H_2O)
1620.95-1532	1004.01		----
1641-1410	993.22	597-551	3458

gives the typical NMR spectrum of 2-amino 4-hydroxy 6-methyl pyrimidine (AHMPDTC). Two C-H proton of the pyrimidine ring of Dithiocarbamate ligand forms a signal at region between 7.59-8.2 ppm and the methyl group protons of pyrimidin ring appear at 2.57ppm in the spectra one more singlet appeared in the region 7.48 ppm and 3.25ppm was due to NH proton in thiouroid region and OH proton of dithiocarbomate ligand..

shows the typical NMR spectrum of Ru metal complex. In the complexes signal due to proton bonded to Nitrogen in the Thioureide bound was observed in the 7.4 to 7.61 ppm. The down field shift of the complex may attributed to an increase of the - bond character and the delocalization of electron along the C-N bond contributed by the substituents and also by the bidentate nature of the dithiocarbamate ligand[20,22,25]. On complexation, the electron density on – NH decreases, the precessional frequency of proton bonded to Nitrogen increases, hence the singal in shifted to down field regions[1,23,24]. High NH stretching indicates as increased C-N double bond character which is due to a greater electron density on the – NCCS moiety[1].

The signal at 6.3-7.65 ppm in NMR spectra of the case of Ru Metal complex indicates the CH protons of pyrimidine ring and broad signals in the range 8.53 ppm in the case complexation of water molecule to metal ion, it was not observed in the case of free ligand one more singlet signal appear at 2.59 ppm repragent metyle group proton on pyramidine ring

2.4.2: NMR Spectral Ananlysis of 2-amino 3-hydroxy 6-methyle Pyramidine Dithiocarbamate(AHMPYDTC) Metal Complexes

Compound	H–N–C (thiureide bond)	(H_2O) Co-ordinated water
AHMPDTC	7.4	------
$(AHMPDTC)_2Ru$	7.61	8.53

Ultra violet –visible spectral ananlysis of 2-amino 3-hydroxy 6-methyle pyramidine dithiocarbamate (AHMPYDTC) Metal Complexe

The solution electronic spectra of the ligand and the complexes were recorded in DMF as solvent in the UV-Visible region. The electronic transition data was given in the Table.2.4.3

Fig. shows the electronic spectra of the Sodium salt of 2-Amino,4-Hydroxy,6-methyl Pyrimidine dithiocarbomate ligand , it shows an one intense absorption bands at 310.45 nm These band may be due to * and n* transitions of N——C——S group and S——C——S [1, 28]. On complexatin these bands were shifted. In all the complexes, bands below 300 nm were attributed to the intra ligand transitions [6,31].

The Electronic spectrum of the Ru-AHMPYDTC complex was shown in the Fig.. The Ruthenium complex shows two intense bands observed at 254.75nm and 318.25 nm were assigned to the intramolecular charge transfer of ligand (* and n* in the N-C = S group). The complex shows two less intense broad bands in the high wave length region corresponding to intraligand d d metal orbital's transitions. In particular this broad band can be assigned to the d_{xy} $d_x^2 - _y^2$ and $d_{xz,\ yz}$ $d_x^2 - _y^2$ transitions. A Moderately intense peak observed at 432 nm may be due to the ligand-metal charge transfer[16].

Table.2.4.3: UV-Vis spectral data of the ligand AHMPDTC and its metal complexes

Compound	$_{max}$/nm	Possible assignment
L = AHMPDTC	310.45	π -π *, n- π *
$[Ru(L)_2(H_2O)_2]$	254.75	π -π* n - π *
	318.25	π -π*, n -π *

THERMAL ANALYSIS OF 2-AMINO 3-HYDROXY 6-METHYLE PYRIMIDINE DITHIOCARBAMATE(AHMPYDTC) METAL COMPLEXES.

International Journal Series

ISSN 2379-1527

TG techniques were employed to follow the thermal behavior of complexes. According to the results obtained, the complexes are not volatile and their decomposition occurs in more than one step. The typical thermogram of complexes. Thermogravimetric studies on the complexes confirmed their proposed molecular formulae. The thermal decomposition of metal complexes has been followed up to 1000°. The decomposition behavior of the complexes was observed in nitrogen atmosphere. The experimental mass losses were in good agreement with the calculated mass loss values which were summarized in the Table.

The thermogram of the Ru complex of AHMPYDTC shows First stage of decomposition around 98.448°C to 154.948°C, which indicates the presence of coordinated water molecules and this decomposition corresponds to small endothermic dehydration of the complex and gives anhydrous complex[11,50,84]. The second decomposition stage with one broad exothermic peak corresponds to the degradation of ligand moiety in the region 287.948°C to 364.948°C forming $M(SCN)_2$ intermediate[5,38,52]. This on subsequent stages undergoes exothermic decomposition to give the corresponding RuS [12,16,51] as the final decomposition product at a high temperature above 442.448-594.948°C

2.4.4: Thermal Ananlysis data of 2-Amino 3-Hydroxy 6-Methyle Pyramidine DithioCarbamate(AHMPYDTC) Metal Complexes

Complex X=H_2O	Temperature range in °C	Probable assignment	Mass loss (%)	Total mass loss (%)
RuL_2X_2 L=$C_7H_7N_2S_2O$	98.44-154.94 278.94-364.94 442.44-594.94	Loss of $2H_20$ molecules Decomposition of L Formation of RuS	8.83 53.54 21.24	83.61

ESR Spectral Analysis of 2- Amino, 6-Methyle Pyrimidine Dithiocarbamate Metal complexes

ESR spectra obtained for copper complex in DMF at liquid nitrogen temperature and representative ESR spectrum was presented in Fig. In this low temperature spectrum, three peaks of small intensity have been identified which are considered to originate from g|| component. The spin Hamiltonian, orbital reduction and bonding parameters of the complex were given in Table.

Kivelson & Neiman[58] have reported that g|| value is less than 2.3 for covalent character and it is greater than 2.3 for ionic character of the metal–ligand bond in complex, applying this criterion, the covalent bond character can be predicted to exist between the metal and the ligand for complex[35].

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The g tensor value of the copper complex can be used to derive the ground state[35,45]. The trend $g\| > g_{ave} > g\perp > 2.0023$ observed for the complex suggests that the unpaired electron was localized in $d_x^2–_y^2$ orbital[16,46] of the copper (II) complex. The lowest g value (>2.0027) also consistent with $d_x^2{}_y^2$ ground state. The g||/A|| quotient value was 107.10 cm^{-1}, evidence in support of the octahedral geometry with no appreciable distortion.

The Axial symmetry parameter G value was calculated by using the expression, $G = g\|–2/g\perp–2$ and related to the exchange interactions between metal-metal centers, according to Heathway[83], for the present complex the G=4.4065, indicates the formation of monomeric complexes [42]. The ESR parameters g||, g⊥, A||*, and A⊥* of the complex and the energies of d–d transitions were used to evaluate the orbital reduction parameters (K||, K⊥). According to Hath way the observed K|| < K⊥ indicates the presence of significant in plane Π–bonding[83]. The molecular orbital coefficients or the bonding parameters a^2 (in plane a–bonding) and b^2 (in plane π–bonding) were calculated [36]. The observed $\acute{\alpha}^2$ value for the present chelate 0.8324 indicates that the complex was having some covalent character.

The reduction of P value from the free ion value (0.036cm^{-1}) might be attributed to the strong covalent bonding[47]. The Fermi constant interaction term (K) indicates the interaction between the electronic and the nuclear spins[80] give n by the expression K=Ao/(P–Ago), where (Ago= g_e–go), it represents the amount of unpaired electron density at the nucleus[45] The lower P and a^2 values for Ru [AHMPYDTC] complex suggest the presence of strong in–plane FI bonding which in agreement with higher ligand field. The shape of ESR lines,

ISSN 2379-1527

ESR data together with the electronic spectral data suggest octahedral geometry for Ruthenium complex [48],

Table 2.4.5. Spin Hamiltonian and orbital reduction parameters of Ruthenium complex in DMF solution

Parameters	Ru (AHMPYDTC)
g‖	2.0565
g⊥	2.0146
g_{ave}	2.0186
G	4.4065
A‖*	0.0192
A⊥*	0.0203
A^*_{ave}	0.0200
K‖	0.0236
K⊥	0.0258
P*	0.0035
α^2	0.8324

* Values are given as cm^{-1} units

CONDUCTIVITY MESUREMENT OF 2-AMINO 3-HYDROXY 6-METHYLE PYRAMIDINE DITHIOCARBAMATE (AHMPYDTC) METAL COMPLEXES

The molar conductance of complex in DMF ($3X10^{-3}$ M)was determined at $27+2^0$C using systronic 303 direct reading conductivity bridge.

The specific and molar conductance value were calculated. If molar conductance value is more than 20 $Ohm^{-1}.cm^{-1}$the metal complex are said to beelectrolytic in nature .if the k value is less 20 Ohm^{-1} Cm^{-1} the metal complex are said to be non electrolytic in nature[9].

The conductance values of all metal complexes were given in the table ;; molar conductance value for all the newly synthesized complexes were in the range 333-747 Ohm^{-1} Cm^2, mol^{-1} the molar conductance of all metal complexes shows them to be electrolytic in nature.[26,29.]

Table. 2.4.6. Conductance data for M [AHMPYDTC] complexes

(with cell constant 1.01) Metal Complex	Conductance (Ohm's)
$[(AHMPDTC)_2(H_2O)_2]$ Ru	0.74

Specific conductance ($Ohm^{-1}.cm^{-1}$)	Molar conductance ($Ohm^{-1}.cm^2.mol^{-1}$)
0.74	747

Magnetic susceptibility measurement of 2- Amino, 6-Methyle Pyrimidine (AHMPYDTC) Dithiocarbamate Metal complexes

The effective magnetic moment values for the complexes were presented in the Table.2.4.7 The magnetic moment of the Cu complex was 1.90 B.M. This value suggests the formation of octahedral complex[34,36]. The present synthesized. Ru complexes shows magnetic moment 1.45, 7.76, 1.85 ,6.67, 1.83, 5.56, 1.83, and 4.78 B.M.

Table. 2.4.7. Magnetic susceptibility data of 2-Amino,6-Methyle Pyrimidine (AHMPYDTC) Dithiocarbamate (AHMPYDTC) Metal complexes

Metal Complex	Magnetic moment(B.M)
$[(AHMPYDTC)_2(H_2O)_2]$ Ru	4.78

Powdered X-Ray diffraction analysis of 2- Amino, 6-Methyle Pyrimidine (AHMPYDTC)Dithiocarbamate Metal complexes.

The X-Ray diffractogram of M [AHMPYDTC] Complexes were shown in the Fig.. to Fig.. which were ranging 2 between 5-50 Where θ is the Bragg's angle. All the main peaks were indicated and calculated values of Miller indices (h k 1) along with observed d–specified and 2θ were specified in the Table. All the peaks have been indexed and 2θ values compared in graph. Comparison values reveal that there was good agreement between values of 2θ and d–values. The powder X–ray diffraction data showed identical features[69] with very poor crystallinity. The patterns were qualitative and dispersive in intensity for Cu and Ru metal complexes. The XRD patterns were used to explain qualitatively the degree of crystallinity. The diffraction patterns of the complex had been indexed by standard methods and the (h k 1) values were calculated from the indexed data by trial and error method.

Table :2.4.9: Powder X-Ray diffraction data of Ru [AHMPYDTC]complexe

Exp-d	Cal – d	Exp - 2θ	Cal - 2θ	h	k	l
6.8594	6.859432	12.8955	12.8953	1	2	0
5.0302	5.030235	17.6172	17.6167	3	1	1
4.8121	4.8121	18.4223	18.4219	3	2	2
4.6486	4.6485	19.0761	19.0761	3	3	0
4.1663	4.1662	21.3087	21.3086	4	3	0
3.7182	3.7182	23.9125	23.9124	4	1	0
3.3815	3.3814	26.3346	26.3345	4	2	1
3.1864	3.1863	27.9791	27.9790	4	2	2
3.0184	3.0183	29.5708	29.5707	4	0	0
2.8122	2.8122	31.7936	31.7935	5	1	0

IV. CONCLUSIONS

Ru complexe of 2-Amino 4-Hydroxy 6-methyle pyramidinedithiocarbamate with have been synthesized and characterized. The ligand moiety exhibit a bidentate coordination mode in the Ru(III) complex. Solid reflectance

International Journal Series

ISSN 2379-1527

spectra and magnetic data indicate that the complexes are Paramagnetic and Octahedral. The complexesshow selective activity towards some of the test microorganisms.

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ISSN 2379-1527