

Synthesis, Spectro Chemical Behaviour of Novel Heterocyclic Dithiocarbamate Metal Complexes – Biological Activity

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Abstract: The synthesis and investigation of new Hetero Cyclic Dithiocarbamate ligand and its solid metal complexes derived from 4-Amino-1,2,4- triazole(ATAZ) and 2-Amino 4-Hydroxy-6-methyl pyrimidine (AHPY) by using different synthetic methods. The derived colored complexes are Au (III) and Ru (III) with above mentioned ligands. The structures and bio cancer activity were elucidated by different type of structural techniques like Elemental analysis, IR, NMR, UV-Vis Spectrometry, ESR, TG-DTA and Conductometric measurements. In addition the authors have been screened the compounds for biological activity and cancer activity of Au, Ru complexes. It was found that the compounds have shown activity against bacteria and cancer viruses.

Keywords: Synthesis, Characterization, Dithiocarbamate metal complexes, 4-Amino-1,2,4-triazole, 2-Amino 4-hydroxy-6-methyl pyrimidine.

I. Introduction

The Dithiocarbamates are the most versatile and thoroughly studied ligand in coordination chemistry. Metal complexes of dithiocarbamates have been reported as antitumor, antibacterial and antifungal agents. Transitional metal complexes with schiff base ligands have been prepared in view of their potential applications as antibacterial and antifungal drugs. The importance of dithiocarbamate base ligands and their complexes with transitional metal have been enhanced especially due to their biological applications. Carbamates are very good complexing agents. A perusal of literature survey reveals that the field of Schiff base metal complexes is vast and fast developing on account of numerous applications in various important fields and the wide variety of structures possible for the ligands depends in group on the amines. Metal complexes of dithiocarbamate and their applications have been widely investigated during the past years^{1,2}. Dithiocarbamate metal complexes have been used as pesticides^[3], as antiviral and antibacterial agents^{4,5} and as catalysts⁶⁻⁸. The thermal behavior of transition metal complexes of dithiocarbamate has been widely investigated⁹⁻¹¹. The applications of such complexes depend to a large extent on their molecular structure. The author in the present study provides a new series of metal complexes of Au (II) and Ru(II) with carbamate ligand derived from 2-amino 1,2,4-triazole, 2-amino 4-hydroxy 6-methyl pyrimidine. These complexes were characterized by elemental analysis, IR, NMR, UV- Vis Spectrometer, ESR, TGA-DTA and Conductometric measurements to determine the mode of bonding and geometry, biological and anticancer activities of the ligands and metal complexes were also carried out.

II. Materials And Methods

Instrumentation: The percentage compositions of the elements (CHNO) for the compounds were determined using an element analyzer CHNO model Fison EA 1108. The Infra red spectra were recorded as potassium bromide (KBr) discs using a JASCO FT/IR-5300. The ¹H (400Hz) nuclear magnetic resonance spectra were recorded using the ACF200 Broker Germany Spectrometer. Ultraviolet Spectra were recorded using Perkin-Elmer lab India UV-Vis Spectrometer. The Electron spin resonance spectra were recorded using the JES-FA Series and TG-DTA spectra were recorded using the SPTQ600 PA, Thermo gravimetric analyses of the metal complexes were carried out by using the Perkin Elmer system in thermal analysis centre Stick Cochin and ethyl alcohol were used as solvent. All chemicals used in the present investigation were pure Aldrich chemicals.

Preparation of the ligand and its metal complexes: (2-amino- 1, 2, 4,-triazole and 2-amino 4-hydroxy 6-methyl pyrimidine dithiocarbamate and their metal complexes)

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.

For the Preparation of Au (III) and Ru (III) metal chloride salts were used. Dissolve 3.2947g (0.01 Mole) of newly synthesized ligand in adequate of methanol. To this solution, aqueous solution of 0.01 moles of corresponding metal chlorides, and 1 ml of trimethyl amine. The mixture was stirring 6 hours on magnetic stirrer in room temperature. Dark colored (Ru complex), brown colored (Au complex) precipitated were separated out. The coloured metal complexes were washed with water and then methanol, and were recrystallised from ether Table-1-2

Table-1: Analytical data of the ATADTC ligand and their metal complexes

			Complex		
			ATADTC	Au(ATADTC) ₂ X ₂	Ru(ATA) ₂ X ₂
Molecular weight			182.97	555.24	460.18
Colour			LightPink	Brown colour	Dark brown
Yield			86	68	64
M.P			112-113	162-163	182-183
Elemental Analysis	C %	Calculated	19.78	12.97	15.67
		Found	19.76	12.85	15.56
	H%	Calculated	1.66	8.34	10.08
		Found	1.62	8.214	10.00
	N %	Calculated	30.75	20.16	24.37
		Found	30.46	20.05	24.23
	S%	Calculated	35.20	23.08	27.89
		Found	35.00	23.00	27.79
	M%	Calculated	-	35.44	21.98
		Found	-	35.23	21.89

Table-2: Analytical data of the AHMPYDTC ligand and their metal complexes

			Complex		
			AHMPYDTC	Au(AHMPYDTC) ₂ X ₂	Ru(AHMPY) ₂ X ₂
Molecular weight			207.97	601.47	505.58
Colour			Pink Colour	Light brown	Dark
Yield			76	73	68
M.P			132-113	186-187	192-193
Elemental Analysis	C %	Calculated	34.61	23.96	28.51
		Found	34.51	23.78	28.45
	H%	Calculated	2.42	2.01	2.39
		Found	2.32	2.00	2.32
	N %	Calculated	13.45	9.31	11.08
		Found	13.24	9.22	11.02
	S%	Calculated	30.80	21.32	25.38
		Found	30.75	21.12	25.23
	M%	Calculated	--	32.75	19.99
		Found	--	32.44	19.86

III. Result And Discussion

Infrared spectral analysis:

Infrared spectra were recorded with a JASCO FT/IR-5300 Spectrometer (4000-400cm⁻¹) using KBr pellets. By utilizing this spectroscopy, the presence of important functional groups in the compound can be identified. Table3-4 through light on the observation made in analyzing IR spectra of ligand and metal complexes.

Infrared Au (III) and Ru (III) complexes of ATADTC and AHMPYDTC :

The Infrared spectrum of the ligand was compared with the spectra of Au(II) and Ru(II) complexes. The data was summarized in table along their assignment. The typical IR spectra were shown in Table 3. The IR

spectrum of the ligand has shows broad band at 1447 cm^{-1} ¹⁴, which was assigned to due $\nu\text{N}=\text{C}-\text{S}$ stretching of Thiouredide bond. In complexes this band was shifted to higher regions, 1498 cm^{-1} and 1462 cm^{-1} ¹⁵ for Au(III) and Ru(III) complexes respectively, suggesting the involvement of azomethine group($>\text{C}=\text{N}$) group in complexation. This was due to the reduction of electron density on Nitrogen. There by indicating the coordination of the metal in through the nitrogen atoms.

The IR spectra of metal chelates shows the disappearance of the $\nu(\text{OH})$ ¹⁶ bond at 3303 cm^{-1} . It indicates the proton displacement from the phenolic (OH) group on complexation. Thus bonding of the metal ions to the ligands under investigation takes place through a covalent link with oxygen of the phenolic group. The IR spectra of Au(III) and Ru(III) metal complexes exhibit a broad band¹⁷ around 3409 cm^{-1} and 3361 cm^{-1} respectively, which can be assigned to $\nu(\text{OH})$ of water molecules associated with complex formation. The two weaker bands at 419.50 cm^{-1} and 460 cm^{-1} were attributed to M-S Stretching vibrations of coordinated water molecules. New bands were observed in the complexes, which were not observed in ligand. AHMPYDTC ligand and its metal complexes are indicate in Table-3.

Table-3: The important IR bands of the Ligand and their Metal Complexes of ATADTC

Compound	OH(Water)	νNCS	νNH	$\nu\text{M-S}$
ATADTC	-----	1447	3461	----
Au(ATADTC) ₂ X ₂	3409	14098	3461	419.50
Ru(ATADTC) ₂ X ₂	3361	1462	3361	460

Table-4- The important IR bands of the Ligand and Their Metal Complexes of ATADTC

Compound	OH(Water)	νNCS	νNH	$\nu\text{M-S}$
AHMPYDTC	-----	1443	3404.32	----
Au(AHMPYDTC) ₂ X ₂	35628	1454.82	3359	562.43
Ru(AHMPYDTC) ₂ X ₂	3458	1456.52	3458	597.16

NMR Spectrum of ATADTC and AHMPYDTC Ligands and Their metal Metal complexes:

The ¹H NMR spectra of ligand and metal complexes in DMSO-d₆ as solvent were given in the spectral technique The chemical shift values of the ligand and metal complexes were shown in Table-5. Ligand shows singlet at 7.2 and 6.74 ppm²¹, which is due to protons bonded to HNC bond of dithiocarbamate ligand. On complexation this band was shifted to high field regions 7.28ppm and 7.32ppm for Au complexes and 7.42 and 7.28 for Ru complexes respectively. This shifting indicates the delocalization to localization of thiouredide bond. The coordinated water molecule on the complex indicate 9.8 for Au complexes and 10.25 and 9.9 for Ru complexes respectively. All types of proton signals given in the below Table -5.

Table-5: ¹H NMR Spectrum of the ligands and its metal complexes in DMSO-d₆ in ppm

Compound	H-N-C	O-H(H ₂ O)
ATADTC	7.2	-
Au(ATADTC) ₂ X ₂	7.28	9.8
Ru(ATADTC) ₂ X ₂	7.4	10.25
AHMPYDTC	6.74	
Au(AHMPYDTC) ₂ X ₂	7.32	9.8
Ru(AHMPYDTC) ₂ X ₂	7.28	9.9

Conductivity measurements:

The molar conductance of complexes in DMF (~10⁻³ M) was determined at 27+20C using Systronic 303 direct reading conductivity bridge. A known amount of solid complexes is transferred into 25ml standard flask and dissolved in dimethyl formamide (DMF). The contents are made up to the mark with DMF.

The complex solution is transferred into a clean and dry 100ml beaker. The molar conductances of the complexes were less than 20 Ohm⁻¹ cm² mol⁻¹ indicating the Non-electrolytic nature. These values suggest non-electrolytic nature of the present complexes. The molar conductance values of these metal complexes are given in the Table 6.

Table-6: Conductance data for metal Complexes: Cell constant: 1.00

S.No	Metal complexes	Conductance Ohm ⁻¹	Specific conductance Ohm ⁻¹ cm ⁻¹	Molar conductance Ohm ⁻¹ cm ² mol ⁻¹
1	Au(ATADTC) ₂ X ₂	0.55	0.55	555
2	Ru(ATADTC) ₂ X	0.54	0.54	545
3	Au(AHMPYDTC) ₂ X ₂	0.76	0.76	767
4	Ru(AHMPYDTC) ₂ X ₂	0.74	0.74	747

Electronic spectra:

In UV-Visible electromagnetic radiation, the transitions are associated with the electronic energy levels of the compound under investigation. The electronic spectra were recorded on a Thermo Spectronic Heylosa spectrophotometer. The transition metal ions occur in a variety of structural environments. Because of this, the electronic structures are extremely varied. The electronic structures have been identified with UV-Visible spectroscopy ATADTC and AHMPYDTC and its metal complexes:

The electronic spectral of ligand and its metal complexes were given in the transitions were reported in the Table-7. Ligand shows signal band at 292 nm, assigned to $\pi-\pi^*$ transition. In complexes this band was shifted to higher wavelength regions. New bands were observed in the complexes at corresponding to the charge transfer transitions. In high concentration spectra of complexes d-d transitions were observed in visible region.

Table-7: Electronic spectral data

S.NO	Complex	λ_{max} of the ligand	λ_{Max} of the complex
1	Au(ATADTC) ₂ X ₂	308.23	322.43
2	Ru(ATADTC) ₂ X ₂	308.23	322.43
3	Au(AHMPYDTC) ₂ X ₂	310.45	322.45
4	Ru(AHMPYDTC) ₂ X ₂	310.45	318.25

Electronic spin resonance spectra:

In the present study the X-band (9.3GHz) ESR spectra of Au (III) and Ru(III) complexes in DMF were recorded at room temperature and at liquid nitrogen temperature (LNT) on a JES-FA SERIES spectrometer. DPPH radical was used as a field maker

Analysis of ATADTC through ESR spectra of Au (III) and Ru (III) complexes:

The ESR spectra of the complex in poly crystalline state exhibit only one broad signal, which is attributed to dipolar broadening and enhanced spin lattice relaxation. Anisotropic Spectra obtained for these complexes in DMF at LNT and representative ESR spectra of Au (II) complexes were presented. In this low temperature spectrum, four peaks of small intensity have been identified which are considered to originate from g_{\parallel} component

The spin Hamiltonian, orbital reduction and bonding parameters of the A (III) complex was presented in Table 8. The g_{\parallel} and g_{\perp} are computed from the spectrum using ATADTC free radical as g marker. Kvelson&Neiman²³ have reported that g_{\parallel} value is less than 2.3 for covalent character and is greater than 2.3 for ionic character of the metal-ligand bond in complexes. Applying this criterion, the covalent bond character can be predicted to exist between the metal and the ligand complexes^[24]. The trend $g_{\parallel} > g_{ave} > g_{\perp}$ observed for the complex suggest that the unpaired electron is localized in dx^2-y^2 and dz^2 orbital of the Au (III) ions for the complex. It is observed that G value for these complexes are greater than four and suggest that there are no interactions between metal-metal centers in DMF medium.

The ESR parameters g_{\parallel} , g_{\perp} , A_{\parallel}^* and A_{\perp}^* of the complexes and the energies of d-d transitions are used to evaluate the orbital reduction parameters (K_{\parallel}, K_{\perp}) the bonding parameters (α^2), the dipolar interaction (P)^[25]. The observed $K_{\parallel} < K_{\perp}$ indicates the presence of out of plane π -bonding. The α^2 values for the present chelates lie in the range 0.42-0.48 and support the covalent nature of these complexes. Giordano and Bereman suggested the identification of bonding groups from the values of dipolar term P . The reduction of P values from the ion value (0.036cm^{-1}) might be attributable to the strong covalent bonding. The values of P obtained for the present complexes in between $0.029-0.036\text{cm}^{-1}$ and remain consistent with bonding of metal ions to sulphur and nitrogen donor atoms respectively. The shape of ESR lines, ESR data together with the electronic spectral data suggest an octahedral geometry for these complexes²⁶.

Table-8-11 : Spin Hamiltonian and orbital reduction parameters of Au and Ru complexes in DMF

Parameters	Au(ATADTC) ₂
g_{\parallel}	2.04559
g_{\perp}	1.99000
g_{ave}	2.00853
G	3.8201
A_{\parallel}^*	0.0182
A_{\perp}^*	0.0022
A_{ave}^*	0.0081
d-d	13500
K_{\parallel}	0.8891
K_{\perp}	0.9824
P^*	0.036
α^2	0.420

Parameters	Ru (ATDTC)
$g_{ }$	2.0845
g_{\perp}	2.0212
g_{ave}	2.0749
G	4.3492
$A_{ }^*$	0.0196
A_{\perp}^*	0.0314
A_{ave}^*	0.0311
$K_{ }$	0.0347
K_{\perp}	0.0369
P^*	0.0046
α^2	0.5987

Parameters	Au (AHMPYDTC)
$g_{ }$	2.5567
g_{\perp}	1.0645
g_{ave}	1.9788
G	2.7265
$A_{ }^*$	0.0192
A_{\perp}^*	0.0213
A_{ave}^*	0.0202
$K_{ }$	0.0212
K_{\perp}	0.0244
P^*	0.0035
α^2	0.2468

Parameters	Ru (AHMPYDTC)
$g_{ }$	2.0435
g_{\perp}	2.0126
g_{ave}	2.0166
G	4.3065
$A_{ }^*$	0.0182
A_{\perp}^*	0.0202
A_{ave}^*	0.0100
$K_{ }$	0.0226
K_{\perp}	0.0248
P^*	0.0025
α^2	0.8224

Magnetic susceptibility measurements of Gold (III) and Ruthenium (III) complexes:

The effective magnetic moment values for all the complexes are represented in the Table.12. There are considerable orbital contribution and effective magnetic moments for octahedral complex at room temperature. The magnetic moments of the present (ATADTC)₂Au and (ATADTC)₂Ru complexes are 4.82 B.M. and 5.3 B.M. and the value is less than the spin only value, it shows reduced Para magnetism, which suggest the formation of low-spin complex having octahedral geometry. The magnetic moments of the present (AHMPYDTC)₂Au and (AHMPYDTC)₂Ru complex are 1.71 B.M. and 4.81 this values are less than the spin-only value, showing reduced para magnetism, which suggest the formation of low-spin complex having square plane.

Table-12: Magnetic moments of Au and Ru

S.No.	Metal Complexes	Effect. In B.M.		Number of unpaired electron
		Theoretical	Observed	
1.	Au(ATADTC) ₂	4.87	4.82	4
2.	Ru(ATADTC) ₂	5.5	5.32	4
3.	Au(AHMPYDTC) ₂	1.83	1.79	1
4.	Ru(AHMPYDTC) ₂	4.87	4.81	4

Thermal analysis:

The thermal studies of these complexes are carried out to know the stability of the complexes on thermal decomposition, as well as to know the different final products that are obtained in thermal decomposition having novel catalytic properties.

Thermogravimetric analysis by ATADTC and AHMPYDTC of Au (II) and Ru (II) Metal complexes:

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

thermo grams of complexes were shown in the Table-13 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 Gold complex of ATDTC shows three main decomposition stages, and the first stage with small endothermic dehydration step in the range of 88.678°C to 123.678°C was due to loss of two water molecules coordinated to the metal . The Second step involves two sub steps which involves decomposition of the ligand moiety, Exothermic decomposition of the ligand moiety takes place around 173.678–213.678°C, to give the stable intermediate M (SCN)₂ and this was stable up to 401.178°C, which on further undergoes exothermic decomposition in the region 401.178–576.178°C in the third stage forming Auric sulphides (AuS) as final residual product .

The thermo gram of the Ru complex of ATDTC shows First stage of decomposition around 92.98°C to 165.48°C, which indicates the presence of coordinated water molecules and this decomposition corresponds to small endothermic dehydration of the complex and gives anhydrous complex. The second decomposition stage with one broad exothermic peak corresponds to the degradation of ligand moiety in the region 240.48°C to 292.98°C forming M(SCN)₂ intermediate . This on subsequent stages undergoes exothermic decomposition to give the corresponding Ru as the final decomposition product at a high temperature above 557.98°C.

Table-13 The thermal studies of ATADTC complexes

Complex X=H ₂ O	Temperature range in °C	Probable assignment	Mass loss (%)	Total mass loss (%)
AuL ₂ X ₂ L=C ₃ H ₃ N ₄ S ₂	88.678-123.67	Loss of 2H ₂ O molecules	8.62	78.43
	173.67-271.17	Decomposition of L	51.74	
	401.17-576.17	Formation of AuS	18.07	
RuL ₂ X ₂ L= C ₃ H ₃ N ₄ S ₂	92.98-165.48	Loss of 2H ₂ O molecules	9.62	85.82
	245.48-292.98	Decomposition of L	55.4	
	557.98	Formation of RuS	20.8	

The thermo gram of the Au complex of AHMPYDTC shows First stage of decomposition around 90.508°C to 130.508°C, which indicates the presence of coordinated water molecules and this decomposition corresponds to small endothermic dehydration of the complex and gives anhydrous complex. The second decomposition stage with one broad exothermic peak corresponds to the degradation of ligand moiety in the region 243.008°C to 290.508°C forming M(SCN)₂ intermediate. This on subsequent stages undergoes exothermic decomposition to give the corresponding AuS as the final decomposition product at a high temperature above 348.008-478.008°C.

The thermo gram 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. 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 . This on subsequent stages undergoes exothermic decomposition to give the corresponding RuS as the final decomposition product at a high temperature above 442.448-594.948°C

Table-14 The thermal studies of c AHMPYDTC complexes

Complex X=H ₂ O	Temperature range in °C	Probable assignment	Mass loss (%)	Total mass loss (%)
AuL ₂ X ₂ L= C ₇ H ₇ N ₂ S ₂ O	90.50-130.50	Loss of 2H ₂ O molecules	7.77	80.32
	243.08-290.50	Decomposition of L	53.67	
	348.08-478.00	Formation of AuS	18.88	
RuL ₂ X ₂ L=C ₇ H ₇ N ₂ S ₂ O	98.44-154.94	Loss of 2H ₂ O molecules	8.83	83.61
	278.94-364.94	Decomposition of L	53.54	
	442.44-594.94	Formation of RuS	21.24	

Biological activity:

The author in this present investigation attempted to find out antibacterial activity of ligand and their metal complexes against *Salmonella typhi*, *Enterococcus faecalis* and *Escherichia coli* choosing serial paper disc method Table 15. The results of the biological activity of the metal complexes indicated the following facts. A comparative study of the ligand and their complexes indicates that the metal chelates exhibited higher antibacterial activity than that of the free ligand. The increase in the antibacterial activity of metal chelates was found due to the effect of metal ion on the metal chelates which could be explained on the basis of overtones concept and chelation theory. On chelation the polarity of the metal ion reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charges of metal ion with donor groups. It was further noted that the delocalization of electrons over the whole chelate ring enhanced the lipophilicity of the complexes. This increased lipophilicity³¹ enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganism. The zones of inhibition of the ligand metal complexes were in the Table.15. The activity was compared with zone of inhibition was measured in mm and reported in of Au (II) and Ru(II)Complexes of Swift, is found to be more .

Table 15 Antibacterial Activity of the Metal complexes Total Area of Zone of clearance in mm

S.No.	Compound	Salmonella Typhi	Enterococcus Faecalis	Escherichia coli
1	ATADTC	22	24	25
2	Au(ATADTC) ₂	23	27	26
3	Ru(ATADTC) ₂	26	25	28
4	AHMPYDTC	21	22	23
5	Au(AHMPYDTC) ₂	27	24	24
6	Ru(AHMPYDTC) ₂	24	26	25

IV. Conclusion

The above study results reveals that, it can be concluded that Dithiocarbamate metal complex eses as a very good complexing agent towards many transition metal ions. By using above spectral studies these behave bidentate ligands during complexation. All the metal complexes carry no change and are thermally stable. As such no single technique is independent of predicting final structures of the complexes

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References

- [1]. D. Coucouvanis, Progress in Inorganic Chemistry, Vol. 11 (Ed., S. J. Lippard), John Wiley, New York, 1970.
- [2]. R. Eisenberg, Progress in Inorganic Chemistry, Vol. 12 (Ed., S. J. Lippard), JohnWiley, New York, 1970.
- [3]. D. Coucouvanis, Progress in inorganic Chemistry, Vol. 26 (Ed., S. J. Lippard),John Wiley, New York, 1979.
- [4]. V. F. Plyusnin, V. P. Crivin and S. V. Larionov, Coordination Chemistry Reviews, 159, 121 (1997) and references therein.stari Cxtra-tiono fchelates, Mir, Moscow, 1966, p. 392.
- [5]. IM. Birko, Analytical Reagents. Dithiocarbant,-tes, Nauka, Moscow, 1984,p. 343.
- [6]. M.V.Korablev, Derivative of Dithiocarbanline Acids, Chenistry, Toxicology, Pharnrucology and Clinical Application, Belarus, Minsk, 1971, p. 152.
- [7]. G.D.Thorn and R. A. Ludwig, The Dithiocarbamates and Related Compounds, Elsevier,A msterdam, 1962, p. 298.
- [8]. G. A. Bloch, Organic Accelerators of Rubber Vulcanisation, Khimiya, Moscow,1972, p. 559.
- [9]. V. A. (Irmhotsh~V., I. Klassen and I. N. Plaskin, Flotufion, Nedra, Moscow, 1973, p. 784.
- [10]. D. Coucouvanis, Prog. Inorg. Chem., 11,223 (1970).
- [11]. F. Yu. Rach~nsk~Ai., S. Mozhuchin, N. M. Slovachevskaya and L. I. Tank, Usp. Khiml. 28, 1488 (1959);
- [12]. J. Tomson, Protei,tion of Mammuliu from lowisationIrradiatiorr, Atomizdat, Moscow, 1%4, p. 176.
- [13]. G. Scott (Ed.), Dcuelopn~cnts in Polymer Stabilisation, Part I, Applied Science, London, 1979.
- [14]. Y. L. Goldfarb, E. C. Ostapenko, V. B. Ivanov, A. F. Efremkin and V. L. Litvinov, K INIG.e terotsikl Soedin., 1481 (1982).
- [15]. A.M. Ewald, I<. L. Martin, I. C. Ross and A. t~i. White, Proc. Roy. Soc. (London), A280, 235 (1964).
- [16]. W. E. Hatfield, Inorg. Chem., 22, 833 (1983); L. Qian, P. Sing H. Ro, W. E. Hatfield, Inorg. Chenr., 29, 761 (1990).
- [17]. E. Emmet ReId, Organic Chmristry of Bivalent Sulphur, Vol. IV, Chemical Publishing To., New York, 1962, p. 140.
- [18]. E. Mulder, I. Prakt. Clvnl., 101,401 (1867).
- [19]. J. Chatt, I. A. Duncason and L. M. Venanzi, Naturc, 177, 1042 (1956); (b) Suomen Kemistilehti, 298, 75 (1956).
- [20]. C. J. M. Van der Kerk and H. L. Klopping Rec. Trau. Chim., 71,1179 (1952).
- [21]. M. Colaplelro, A. Domen~canao nd A. Vaciago, Cllr>nC.onrnln., 572 (1968).
- [22]. B. F. C. Johnson and K. H. Al-Obaide, Chetn. Con~nrn.8, 76 (1968).
- [23]. J. Willemse, J. A. Cras, J. J. Steggerda, C. P. Keijzers, Structure and Bonding, Vol. 29, 1977.
- [24]. J. A. Cras and J. Willemse, Recl. Trav. Chint. Pays-Bas, 97, 28 (1978).
- [25]. D. Coucouvanls and J. P. F. Fackler Jr., Inorg. Chnr., 6, 2047 (1967).
- [26]. K. Nakamoto, J. Fujita, R. A. Kondrate and Y. Morimoto, I. Chem. Phys., 39, 423 (1 963).

- [27]. G. Durgaprasad, D. N. Sathyanarayana and C. C. Patel, *Can. I. Chem.*, 47,631 (1969).
- [28]. D. A. Brown, W. K. Glass and M. A. Burke, *Spectrochim. Acta*, 32A, 137 (1976).
- [29]. G. S. Nikolov, *Irrwg. Nucl. Cknr. Lett.* 7, 1213 (1971).
- [30]. C. O'Conner, J. D. Gilbert and G. Wilkinson, *I. Civnr. Soc., A*, 84 (1969).