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RESEARCH PAPER

Synthesis and characterization of Co(II) complexes with ester thiosemicarbazone

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ABSTRACT

Complexes of cobalt (II) of general composition $[ML_2X_2]$, $[ML_2X]X$ were prepared with thiosemcarbazones (L^1, L^2, L^3 and L^4). These complexes were characterized by elemental analysis, molar conductances measurements, Magnetic moments IR, electronic spectra, and EPR spectral studies. All are the nonelectrolyte in nature therefor these complexes may formulated $[M(L)_2X_2]$. All the complexes are of high-spin and show octahedral jeometry.

Key Words : Acetoacetic ester thiosemicarbazone, Isopropyl ester thiosemicarbazone, 6-methyl Pyran-2-one-4 hydroxy 3 diacarboxylic acid ester thiosemicarbazone, Biological activity

View point paper : Kumar, Dinesh, Renu and Mittal, Mradula (2012). Synthesis and characterization of Co(II) complexes with ester thiosemicarbazone. *Asian Sci.*, **7**(1): 110-116.

The biological and medicinal properties of these ligands and their derivatives have gained much interest. Thiosemicarbazones and their 3d-metal complexes have been found to exhibit anti-fungal[1], anti-bacterial[2], anti-viral[3], anti-tubercular[4] and anti carcinogenic activities [5]. The anti-fungal activity of these compunds is due to the presence of toxophyrically important N–C=S moiety[6]. Thiosemicarbazides and their Schiff bases also display anti-tumour [7-8] activity. It is expected that thio ligands will also show variability in structure and bonding in its transition metal complexes. It has been reported that thiosemicarbazide and its complexes with 3d-metal ions show *in vitro* and *in vivo* anti-tumour activity[9].

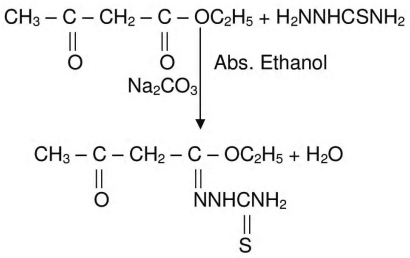
RESEARCH METHODOLOGY

A.R. Grade chemical and fluka reagents were used in the present study. The solvent were purified before use by processing. Semicarbazide hydrochloride, acetoacetic ester, isopropyl ester, methyl ester of 6-methyl Pyran-2-one-4 hydroxy 3 diacarboxylic acid, sodium acetate different metalic salts.

Preparation of ligands:

Preparation of Acetoacetate ester Thiosemicarbazons (L^1):

Hot ethanolic solution of thiosemicarbazide (0.01 mol, 0.91 g) and ethanolic solution of acetoacetic ester (0.01 mol,



Scheme -1

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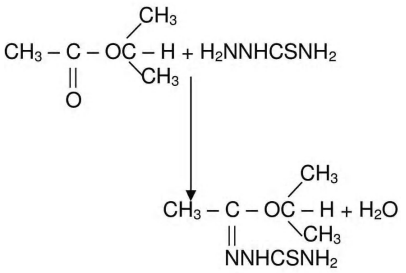
1.183 ml) were mixed slowly with constant stirring. This mixture was refluxed at 75^{0}C for 3-4 hr. On cooling cream precipitate was formed. It was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}. The structure of ligand and scheme for synthesis is shown in scheme 1.

Preparation of isopropyl ester Thiosemicarbazone (L^2):

Hot ethanolic solution of Isopropyl acetate (0.01 mol, 0.849 ml) and thiosemicarbazide (0.1 mol, .91g) were mixed slowely with constant stirring. This mixture was refluxed at 80^{0}C for 2 hr. On cooling, white precipitate was formed. It was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}. The structure of ligand and scheme for synthesis is shown in scheme 2.

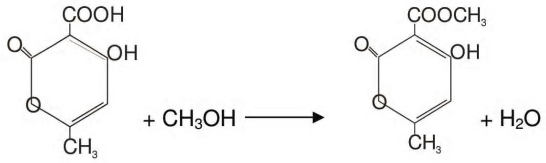


Scheme -2

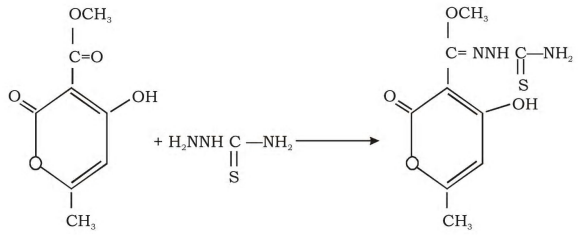
Preparation of Thiosemicarbazone of 6-methyl Pyran-2-one-4 hydroxy 3 diacarboxylic acid [L^3]:

The starting materials 6-methyl Pyran-2-one-4 hydroxy 3 diacarboxylic acid and thiosemicarbazide were purchased Fluka reagents. The ligand was prepared in two steps.

Step 1: 6-methyl Pyran-2-one-4 hydroxy 3 diacarboxylic acid (0.01 mol, 1.70 g) was refluxed with methanol (0.01 mol, 0.25 ml) in the presence 10% sulphuric acid. Thus the ester of 6-Methyl-2H- Pyran-2, 4, (3H) dione-3-carboxylic acid was formed.



Step 2 : 6-methyl Pyran-2-one-4 hydroxy 3 diacarboxylic acid (0.01 mol, 1.84 g) and thiosemicarbazide (0.01 mol, 0.91 g) were refluxed in ethanol for 2 hr at 70-80^{0}C. On cooling light yellow precipitate was formed. It was filtered, washed with cold ethanol and dried under vacuum P_4O_{10}. The structure of ligand and scheme for synthesis is shown in scheme 3.

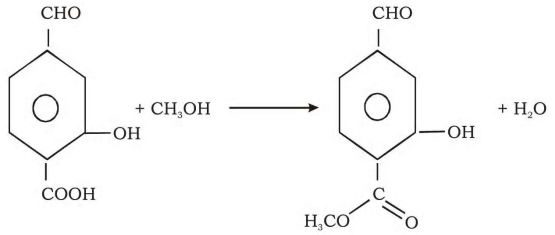


Scheme -3

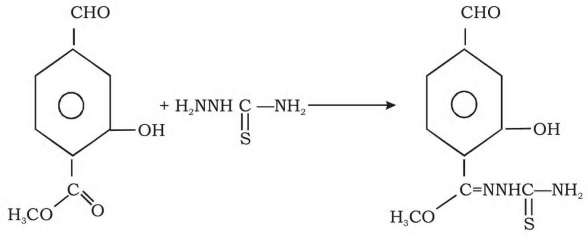
Preparation of 3-Formylmethyl salicylate Thisemicarbazone (L^4) :

The ligand was prepared in two steps :

Step 1 : The 3-formyl salicylic acid (0.01 mol, 1.66g) was refluxed with methanol in the presence of 10% H_2SO_4 for 2 hr. A light yellow colour precipitate, 3-formyl methyl salicylate was formed.



Step 2 : The 3-formyl methyl salicylate (0.01 mol, 1.80 g) thiosomicarbazide (0.01 mol, 0.91 g) in ethanolic solution were refluxed for 2 hr at 75^{0}C. On cooling, white precipitate was formed. It was filtered washed with cold ethanol and dried under vacuum over P_4O_{10}. The structure of ligand and scheme for synthesis is shown in scheme 4.



Scheme -4

Characterization of ligands:

Elemental analysis:

The ligands were found to have the composition as shown in Table 1.

Mass spectra [10-14] : Electron impact mass spectra of the ligands were recorded on TOF MS ES+ Mass spectrometer

Table 1 : Physical and elemental analysis data of ligands

Sr. No.	Elemental formula	Colour	Yield (%)	Melting Point (0^0C)	Molecular weight	Elemental analysis observed (Calculated)			
						C	H	N	S
1.	$C_7H_{13}N_3O_2S$	Cream	65%	198	203	41.10	6.15	20.50	15.56
						(41.37)	(6.40)	(20.68)	(15.76)
2.	$C_6H_{13}N_3OS$	White	64%	192	175	41.00	7.25	24.00	18.12
						(41.14)	(7.42)	(24.00)	(18.28)
3.	$C_9H_{11}N_3O_4S$	Light	70%	200	259	41.99	4.00	16.00	12.15
		Yellow				(42.02)	(4.28)	(16.34)	(12.45)
4.	$C_{10}H_{17}N_3O_3S$	White	76%	197	259	46.00	6.00	16.00	12.00
						(46.33)	(6.56)	(16.21)	(12.35)

from University of Delhi.

Mass spectrum is a presentation of the masses of the positively charged fragments (including the molecular ion) versus their relative concentrations. The more intense peak in the spectrum, called the base peak, is assigned a value of 100% and the intensities of other peaks, including the molecular ion peak are reported as percentages of the base peak. The molecular ion peak may some times the base peak. The molecular ion peaks is usually the peak of highest mass number for the isotopic peaks. The intensities of the isotope peaks relative to parent peak can lead to the determination of a molecular formula. The measured isotope peaks are usually slightly higher than the calculated contribution because of incomplete resolution, bimolecular couoisions or a contributation from the incident peak of ion impurity of the proposed ligands.

Mass spectrum of the ligands :

The mass spectrum of ligand L^l shows the molecular ion peak (M^+) at m/z = 203 amu. The different ions gives the peaks of different mass like 160, 146, 101, 75, 60 and 16. The intensities of these give the idea of stability of ligands

The mass spectrum of Ligand L^2 shows that molecular ion peak (M^+) at m/z=175 amu. The other peaks at 160, 148, 101, 75, 60 and 16 amu. Corrosponds to various fragments show the stability of ligand.

The mass spectrum of Ligand L^3 shows the molecular ion peak (M^+) at m/z=259 amu. The other different ions gives peaks of 132, 101, 75, 60 and 16 amu. The intensities of peaks are in correspondance with the abundance of the ions.

The mass spectrum of Ligands L^4 shows the molceular ion peak (M^+) at m/z=259 amu. The other different ions give the peaks of different mass numbers like 132, 101, 75, 60 and 16 amu. The intesities of these peaks give the idea of stability of ligand.

I.R. spectra[15-32] :

In the present study in IR spectra of ligands the bands appeared at 1560-1595 cm^{-1} and 729-780 cm^{-1} due to ν(C=N) and ν(C=S) groups respectively.

$L^1 \Rightarrow$ Nitrogen atom of ν(C=N) group and oxygen of ν(C=S) group ÞBidentate

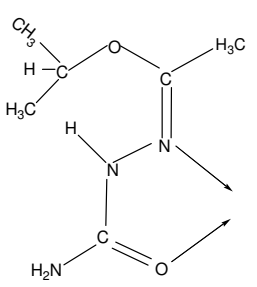
$L^2 \Rightarrow$ Nitrogen atom ν(C=N) group and oxygen of ν(C=S) group ÞBidentate

$L^3 \Rightarrow$ Nitrogen atom ν(C=N) group and atom ν(C=S) group and atom of ν(C=O) phenolic oxygen group $\Rightarrow$ Tridentate

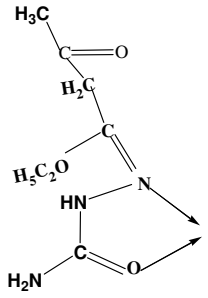
$L^4 \Rightarrow$ Nitrogen atom of ν(C=N) group and oxygen atom of ν(C=S) group $\Rightarrow$ Bidentate

Proposed structure of the ligands :

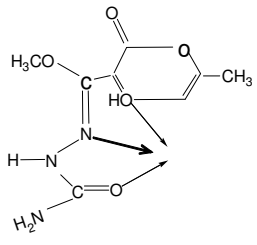
On the basis of elemental analysis, mass and IR spectra the following structure has been assigned for the ligands.



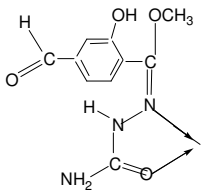
L^1



L^2



L^3



L^4

Preparation of complexes :

All the complexes were prepared by the following method. A hot ethanolic solution of metal salt (0.05 mol) was mixed with hot ethanolic solution of the corresponding ligand

(0.1 mol). The contents were refluxed for about 2 hr. On cooling the contents coloured complex was separated out. The complex was filtered washed with 50 per cent ethanol and dried in a vaccuum desicator.

RESEARCH AND REMONSTRATION FINDINGS

On the basis of the elemental analysis (Table 2) the comlexes have the composition $M(L_2)\ X_2$ (where X=Cl^-, NO_3^- and CH_3COO^-). Molar conductance of the complexes with ligand L^1, L^2, L^3 and L^4 indicates the following nature :

Ligands	Metal salts	Nature of complex	Composition
L^1, L^2, L^4	$CoCl_2.6H_2O$	Non-	$[Co\ (L)_2X_2]$
	$Co(CH_3COO)_2\ 4H_2O$	electrolyte	
	$Co(NO_3)_2\ 6H_2O$		
L^3	$CoCl_2.6H_2O$	1:2	$[Co\ (L)_2]X_2$
	$Co(CH_3COO)_2\ 4H_2O$	electrolyte	
	$Co(NO_3)_2\ 6H_2O$		

Ligands L^1, L^2 and L^4 act as bidentate manner coordinate through N and S atom. On the other hand L^3 acts as tridentate coordinate through N, S and O atoms.

IR spectra of the ligands:

Infrared spectra of ligands and their mode of coordination already have been discussed in ligand synthesis and characterization.

IR spectra of the complexes:

As discussed earlier, the ligands display IR bands in the range 1560-1595 cm^{-1} and 729-760 cm^{-1} which are attribuled to the ν(C=N) and ν(C=S) vibration. On complex formation the position of these bands is shifted to the lower side. This indicates that coordination takes places through the nitrogen atom of ν(C=N) and sulphur atom of ν(C=S) groups.

In addition, the ligand L^3 display bands at 3100 cm^{-1} due to phenolic oxygen and the position of this band is shifted towards ligand side on complextion.

IR spectra of nitrato complexes :

IR spectra of the nitrato complexes bands corresponding

Table 2 : Elemental analysis and molar conductance of cobalt(II) complexes

Sr. No.	Complex	Colour	M. Point (0^0C)	Yield (%)	Molar conductance	Elemental analysis observed (Calculated) C	H	N	M
1.	$[Co\ (L^1)_2\ Cl_2]$	Pink	255	68	12	31.24	4.70	15.56	10.59
	$CoC_{14}H_{26}N_6O_4S_2Cl_2$					(31.34)	(4.85)	(15.67)	(10.99)
2.	$[Co\ (L^1)_2\ NO_3)_2]$	Shiny	259	60	08	28.10	4.30	19.00	10.00
	$CoC_{14}H_{26}N_8O_{10}S_2$	Pink				(28.52)	(4.41)	(19.01)	(10.00)
3.	$[Co\ (L^1)_2\ CH_3COO)_2]$	Pink	260	68	10	37.00	5.35	14.10	10.00
	$CoC_{18}H_{30}N_6O_8S_2$					(37.05)	(5.48)	(14.40)	(10.10)
4.	$[Co\ (L^2)_2\ Cl_2]$	Shiny	285	62	12	35.00	5.31	17.40	12.00
	$CoC_{12}H_{26}N_6O_6S_2Cl_2$	Pink				(30.00)	(5.41)	(17.50)	(12.27)
5.	$[Co\ (L^2)_2\ (NO_3)_2\ ]$	Pink	260	65	10	27.00	4.52	21.00	11.00
	$CoC_{12}H_{26}N_8O_{12}S_2$					(27.02)	(4.87)	(21.01)	(11.05)
6.	$[Co\ (L^2)_2\ (CH_3COO)_2\ ]$	Dark	279	67	16	34.21	6.00	15.56	11.00
	$CoC_{16}H_{32}N_6O_{10}S_2$	Pink				(36.43)	(6.07)	(15.94)	(11.18)
7.	$[Co\ (L^3)_2]\ Cl_2$	Light	270	70	90	33.21	3.05	13.00	9.00
	$CoC_{18}H_{22}N_6O_8S_2Cl_2$	Pink				(33.54)	(3.41)	(13.04)	(9.15)
8.	$[Co\ (L^3)_2\ (NO_3)_2$	Pink	271	68	195	31.20	3.42	16.00	8.23
	$CoC_{18}H_{22}N_8O_{10}S_2Cl_2$					(31.26)	(3.43)	(16.21)	(8.52)
9.	$[Co\ (L^3)_2]\ (CH_3COO)_2$	Pink	269	71	120	37.50	4.12	12.00	8.30
	$CoC_{22}H_{28}N_6O_{12}S_2$					(37.88)	(4.32)	(12.05)	(8.50)
10.	$[Co\ (L^4)_2\ Cl_2]$	Pink	285	62	08	37.25	3.25	13.00	9.00
	$CoC_{20}H_{22}N_6O_6S_2Cl_2$					(37.74)	(3.45)	(13.20)	(9.26)
11.	$[Co\ (L^4)_2\ (NO_3)_2]$	Light	270	70	07	34.53	3.00	10.05	8.50
	$CoC_{20}H_{22}N_8O_{12}S_2$	Pink				(34.83)	(3.14)	(10.25)	(8.55)
12.	$[Co\ (L^4)_2\ CH_3COO)_2]$	Dark	275	65	11	42.00	4.00	12.00	8.52
	$CoC_{24}H_{28}N_6O_{10}S_2$	Pink				(42.17)	(4.09)	(12.29)	(8.62)

to the coordinated nitrate group. The coordinated nitrate group show absorption at 1505-1475 (ν_1), 1325-1275 (ν_5), 1045-1020 (ν_2) and 803 cm^{-1} (ν_6). The complexes under study show IR bands at 1480-1429 cm^{-1} (ν_1), 1345-1274 cm^{-1} (ν_5), 1136-1076 cm^{-1} (ν_2) which indicates that the nitrate group attached as unidentate manner.

IR spectra of acetato complexes :

IR spectra of acetoato complexes with all ligands L^1, L^2, L^4 show bands in the region 1590-1620 cm^{-1} ν (C=O) and 1370-1439 cm^{-1} ν (C=S). It indicate the unidentate nature. On the other hand acetato complex with ligand L^3 shows bands correspondent to free acetate group.

Megnetic moment :

All the complexes show magnetic moments in the range 4.97-5.2 B.M., indicating a spin quartet ground state which is obtained for four coordinate tetrahedral, five coordinate square pyramidal or trigonal bipyramidal and six coordinate octahedral. On the basis of electronic spectral studies the possible geometry of the complexes is evaluated.

Electronic spectra :

The electronic spectra of the complexes (Table 3) under study display three well defined bands in the range 9727-11223 cm^{-1}, 14350-15386 cm^{-1} and 19500-20400 cm^{-1} corresponding to $^4T_{1g}(^4F) \rightarrow {}^4T_{2g}(4F)$ ν_1, $^4T_{1g}(^4F) \rightarrow {}^4A_{2g}(^4F)$ (ν_2) and $^4T_{1g}(^4F) \rightarrow {}^4A_{1g}(^4P)$ (ν_3) transitions characteristic of octahedral geometry[33-34].

EPR spectra :

The EPR spectra of the complexes under study were recorded as polycrystalline sample at Liquid nitrogen temperature, the rapid spin lattice relaxation of Co(II) broadens the lines at higher temperature. g-Values are represented in Table 3. The large deviation of the g-values from the spin only value (g=2.0023) is due to the large angular momentum contribution. These results correspond with the magnetic susceptibilites and electronic spectra as discussed earlier.

Ligand field parameters :

Various ligand field parameters *viz.,* Dq, B, β and LFSE have been calculated and reported in Table 4. Dq values were evaluated by using Orgel diagram[35]. Nephlexautic parameters β has been evaluated by using the equation.

$\beta = B_{complex} / B_{free\ ion}$

where $B_{free\ ion}$ for Co(II) is 1120 cm^{-1}. The values of b lines in the range 0.60-0.70 indicating appreciable covalent character in the complexes.

Proposed structure of the complexes :

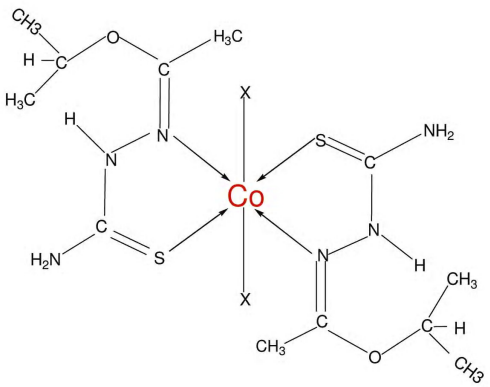
On the basis of elemental analysis, magnetic momement, molar conductance, IR, electronic and EPR spectral studies an octahedral geometry has been assigned for the complexes with ligand L^1, L^2, L^3 and L^4 as follows :

Table 3 : The important IR Bands and their assignment for the ligands

Sr. No.	Ligands	ν (N-H)$^{cm-1}$	ν (C=N)$^{cm-1}$	ν (C=S)$^{cm-1}$	Phenolic oxygen	Nature
1.	L^1	3237	1580	760	-	Bidentate
2.	L^2	3250	1595	729	-	Bidentate
3.	L^3	3258	1560	738	3100	Tridentate
4.	L^4	3258	1578	780	-	Bidentate

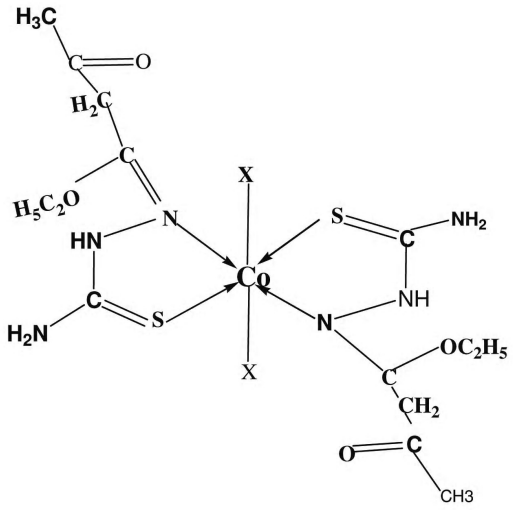
Table 4 : Ligand field parameters and ESR spectral data of Co (II) complexes

Complex	Dq (cm^{-1})	B (cm^{-1})	β	LFSE KJ/mol^{-1}	g_{II}	$g_{\perp}$
$[Co(L^1)_2Cl_2]$	1291	717	0.64	124	3.62	2.32
$[Co(L^1)_2(NO_3)_2]$	1401	778	0.70	134	3.99	2.27
$[Co(L^1)_2(CH_3COO)_2]$	1402	779	0.70	134	4.10	2.14
$[Co(L^2)_2Cl_2]$	1339	744	0.66	128	4.93	2.41
$[Co(L^2)_2(NO_3)_2]$	1269	705	0.63	121	4.13	2.15
$[Co(L^2)_2(CH_3COO)_2]$	1399	778	0.69	134	3.92	2.23
$[Co(L^3)_2]Cl_2$	1385	770	0.69	133	3.96	2.21
$[Co(L^3)_2](NO_3)_2$	1291	717	0.64	124	4.85	2.16
$[Co(L^3)_2](CH_3COO)_2$	1271	706	0.63	121	3.25	2.13
$[Co(L^4)_2Cl_2]$	1295	720	0.64	124	4.27	2.32
$[Co\ (L^4)_2\ (NO_3)_2]$	1300	723	0.65	124	4.76	2.17
$[Co\ (L^4)_2\ (CH_3COO)_2]$	1215	676	0.60	116	4.15	2.13



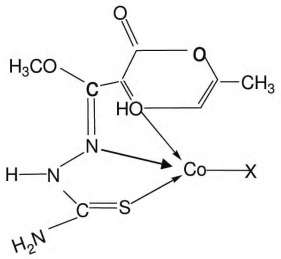
X=Cl^-, NO_3^-, CH_3COO^-

Cobalt complexes of isopropyl ester thiosemicarbazone



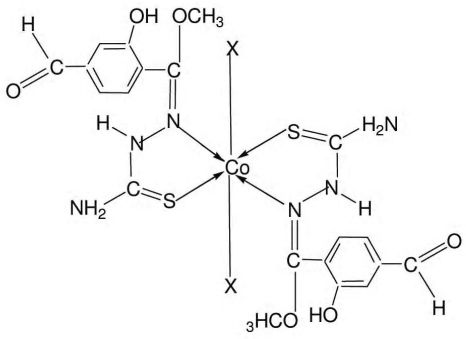
X=Cl^-, NO_3^-, CH_3COO^-

Cobalt complexes of acetoacetate ester thiosemicarbazone



X=Cl^-, NO_3^-, CH_3COO^-

Cobalt complexes of Methyl ester of 6-methyl Pyran-2-one-4 hydroxy 3 diacarboxylic acid thi0semicarbazone



X=Cl^-, NO_3^-, CH_3COO^-

Cobalt complexes of 3-Formylmethyl salicylate thiosemicarbazone

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