

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

■ RENU, DINESH KUMAR AND MRADULA MITTAL

Author for Correspondence -

RENU

Department of Chemistry,
D.A.V. (P.G.) College,
MUZAFFARNAGAR (U.P.) INDIA
dinesh040505@gmail.com

See end of the article for authors
affiliation

ABSTRACT - Complexes of cobalt (II) of general composition $[ML_2X_2]$, $[ML_2X]X$ were prepared with semicarbazones (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 geometry.

Key words - Acetoacetic ester semicarbazone, Isopropyl ester semicarbazone, 6-methyl Pyran-2-one-4 hydroxy 3 diacarbonylic acid ester semicarbazone, Biological activity

How to cite this paper - Renu, Kumar, Dinesh and Mittal, Mradula (2012). Synthesis and characterization of Co(II) complexes with ester thiosemicarbazone. *Asian J. Exp. Chem.*, 7(1) : 45-51.

Paper history - Received : 15.04.2012; Sent for revision : 30.04.2012; Accepted : 08.06.2012

The biological and medicinal properties of these ligands and their derivatives have gained much interest. Semicarbazones 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 compounds is due to the presence of toxophyrically important N-C=S moiety[6]. Semicarbazides 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 semicarbazide and its complexes with 3d-metal ions show *in vitro* and *in vivo* anti-tumour activity[9].

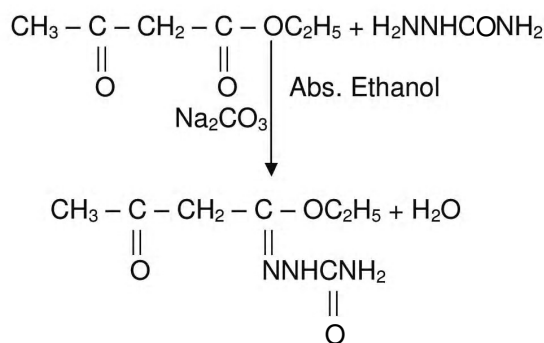
EXPERIMENTAL METHODOLOGY

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 diacarbonylic acid, sodium acetate different metallic salts.

Preparation of ligands:

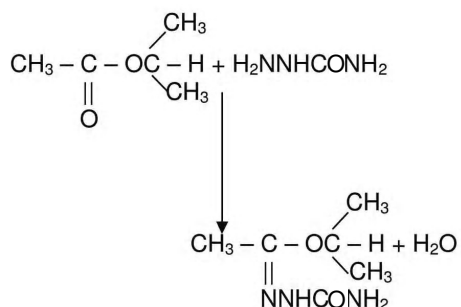
Preparation of Acetoacetic ester semicarbazone (L^1):

Aqueous solution of semicarbazide hydrochloride (.01 mol, 1.12 g) and acetoacetic ester (0.01 mol. of 1.83 ml) were mixed in the presence of sodium acetate (.01 mol, 1.36 g). This solution was stirred with the help of mechanical stirrer for an hour. On cooling a white product was formed, filtered, washed with cold ethanol and dried under vacuum over P_4O_{10} (mt. 180°C yield 68%).



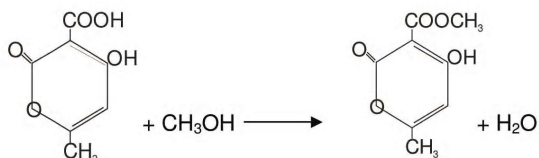
Preparation of isopropyl ester semicarbazone (IESC)(L²):

IESC was prepared by the condensation of isopropyl acetate (0.01 mol, 0.849 ml) with semicarbazide (0.01 mol, 1.12 g) in absolute ethanol. It was purified and recrystallized from the same solvent. The purity was checked by T.L.C. (mp 185°C, yield 80%).

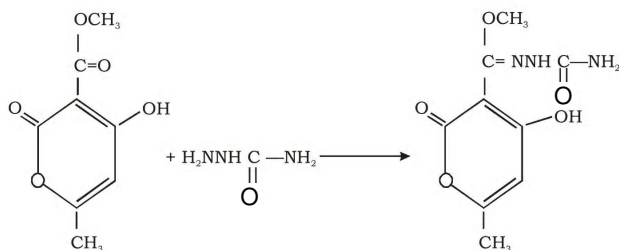

Preparation of semicarbazone of 6-methyl pyran 2-one 4 hydroxy 3 dicarboxylic acid [L³]:

The starting materials 6-methyl-2H Pyran – 2, 4, (3H) dione-3-carboxylic acid and semicarbazide are fluka reagents. The ligands was prepared in two steps :

Step 1 : 6-methyl – 2 H Pyran – 2, 4, (3H) dione – 3 – carboxylic acid (0.01 mol, 1.70 g) was refluxed with methanol (.01 mol, 0.25 ml) in the presence of 10 per cent sulphuric acid. The ester of 6-methyl-2H pyran – 2, 4, (3H) dione – 3 – carboxylic acid formed.

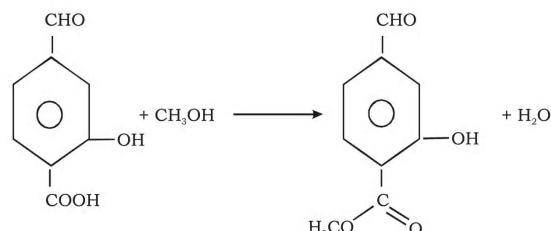


Step 2: The methyl ester of 6-methyl pyran 2-one 4 hydroxy 3 dicarboxylic acid (.01 mol, 1.84 g) and semicarbazide (.01 mol, 1.12 g) were refluxed in ethanol for 1½hr .On cooling yellow colored compound was formed which was filtered, washed with ethanol, dried and recrystallized from ethanol (mp 190°C and yield 70%).

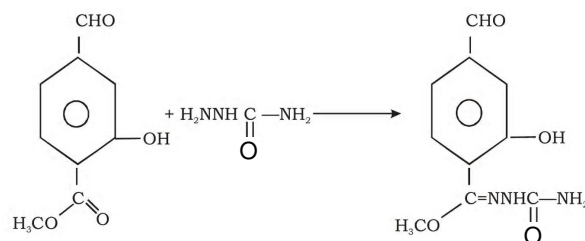

Preparation of semicarbazone of 3-formyl methyl salicylate (L⁴):

The ligand was prepared in two steps :

Step 1: The 3-formyl salicylic acid (.01, 1.66g) refluxed with methanol in the presence of 10 per cent H₂SO₄ for 2 hr a light yellow coloured precipitate of 3-formyl methyl salicylate was formed.



Step 2: The 3-formyl methyl salicylate (.01 mol 1.80g) and semicarbazide (.01 mol 1.12g) in 15 ml of ethanol were refluxed for two hours . After cooling, white solid was separated out. It was filtered, washed with water and dried under vacuum.


Characterization of ligands:
Elemental analysis:

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

Mass spectra [10-14] :

Electron impact mass spectra of the ligands were recorded on TOF MS ES+ Mass spectrometer 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 per cent 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 couisions or a

Table A : Physical and elemental analysis data of ligands

| Sr. No. | Empirical formula | Colour | Yield (%) | Melting point (0°C) | Molecular weight | Elemental analysis % observed (Calculated) | | | |
|---------|---|-------------|-----------|---------------------|------------------|--|----------------|------------------|------------------|
| | | | | | | C | H | N | O |
| 1. | C ₇ H ₁₃ N ₃ O ₂ | White | 68 | 180 | 187 | 44.23 (44.91) | 6.50 (6.95) | 22.15 (22.45) | 25.10 (25.66) |
| 2. | C ₆ H ₁₃ N ₃ O ₂ | Cream | 70 | 210 | 159 | 45.00 (45.28) | 8.20 (8.17) | 25.90 (26.41) | 20.00 (20.12) |
| 3. | C ₉ H ₁₁ N ₃ O ₅ | White | 62 | 197 | 241 | 44.12 (44.81) | 4.20 (4.56) | 17.25 (17.42) | 33.00 (33.19) |
| 4. | C ₁₀ H ₁₁ N ₃ O ₄ | Shiny Cream | 65 | 225 | 237 | 50.50 (50.63) | 4.54 (4.64) | 17.70 (17.72) | 27.00 (27.00) |

contribution from the incident peak of ion impurity of the proposed ligands.

Mass spectrum of the ligands :

The mass spectrum of ligand L¹ 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 L² 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 L³ 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 L⁴ 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] :

The important IR bands and their assignments are given in Table B. In the present study in IR spectra of ligands the bands appeared at 1570-1592 cm⁻¹ and 1672-1695 cm⁻¹ due to ν(C=N) and ν(C=O) groups, respectively.

L¹ ⇒ Nitrogen atom of ν(C=N) group and oxygen of ν(C=O) group ⇒Bidentate

L² ⇒ Nitrogen atom ν(C=N) group and oxygen of ν(C=O) group ⇒Bidentate

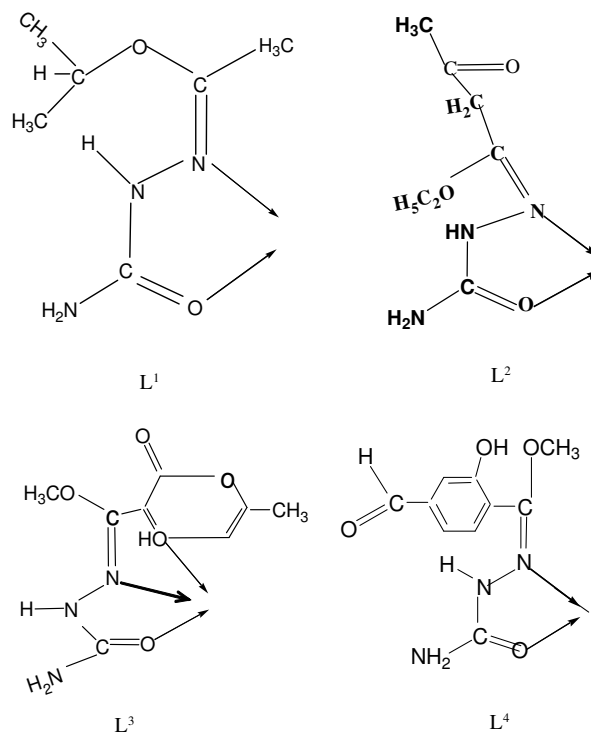
L³ ⇒ Nitrogen atom ν(C=N) group and atom ν(C=O)

group and atom of ν(C=O) phenolic oxygen group ⇒ Tridentate

L⁴ ⇒ Nitrogen atom of ν(C=N) group and oxygen atom of ν(C=O) group ⇒ 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.

**Table B : 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=O) ^{cm-1} | Phenolic oxygen | Nature |
|---------|----------------|-------------------------|-------------------------|-------------------------|-----------------|------------|
| 1. | L ¹ | 3237 | 1570 | 1680 | - | Bidentate |
| 2. | L ² | 3250 | 1585 | 1672 | - | Bidentate |
| 3. | L ³ | 3258 | 1592 | 1695 | 3150 | Tridentate |
| 4. | L ⁴ | 3258 | 1578 | 1687 | - | Bidentate |

| Ligands | Metal salts | Nature of complex | Composition |
|--|---|-------------------|--|
| L ¹ , L ² , L ⁴ | CoCl ₂ .6H ₂ O Co(CH ₃ COO) ₂ .4H ₂ O Co(NO ₃) ₂ .6H ₂ O | Non-electrolyte | [Co (L) ₂ X ₂] |
| L ³ | CoCl ₂ .6H ₂ O Co(CH ₃ COO) ₂ .4H ₂ O Co(NO ₃) ₂ .6H ₂ O | 1:2 electrolyte | [Co (L) ₂] ₂ X ₂ |

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 vacuum desiccator.

EXPERIMENTAL FINDINGS AND ANALYSIS

On the basis of the elemental analysis (Table 1) the complexes have the composition M(L₂) X₂ (where X=Cl⁻, NO₃⁻

and CH₃COO⁻). Molar conductance of the complexes with ligand L¹, L², L³ and L⁴ indicates the following nature :

Ligands L¹, L² and L⁴ act as bidentate manner coordinate through N and S atom. On the other hand L³ 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 attributed 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 L³ display bands at 3100 cm⁻¹ due to phenolic oxygen and the position of this band is shifted towards ligand side on complexation.

Table 1 : Elemental analysis and molar conductance of cobalt(II) complexes

| Sr. No. | Complex | Colour | Yield (%) | M. Point (0°C) | Molar conductance | Elemental analysis found (Calculated) | | | | |
|---------|--|--------|-----------|----------------|-------------------|---------------------------------------|--------|---------|---------|---------|
| | | | | | | C | H | N | O | M |
| 1. | [Co (L ¹) ₂ Cl ₂] | Pink | 65 | 210 | 502.93 | 33.10 | 5.00 | 16.45 | 19.00 | 11.31 |
| | CoC ₁₄ H ₂₆ N ₆ O ₆ Cl ₂ | | | | | (33.40) | (4.85) | (16.70) | (19.08) | (11.71) |
| 2. | [Co (L ¹) ₂ NO ₃] ₂ | Pink | 62 | 225 | 554.93 | 30.10 | 4.00 | 20.00 | 34.50 | 10.51 |
| | CoC ₁₄ H ₂₄ N ₈ O ₁₂ | | | | | (30.27) | (4.32) | (20.18) | (34.59) | (10.61) |
| 3. | [Co (L ¹) ₂ CH ₃ COO] ₂ | Light | 60 | 238 | 550.93 | 39.10 | 5.56 | 15.00 | 29.00 | 10.59 |
| | CoC ₁₈ H ₃₂ N ₆ O ₁₀ | Pink | | | | (39.20) | (5.80) | (15.24) | (29.04) | (10.69) |
| 4. | [Co (L ²) ₂ Cl ₂] | Pink | 70 | 205 | 447.93 | 32.00 | 5.69 | 18.59 | 14.02 | 13.05 |
| | CoC ₁₂ H ₂₆ N ₆ O ₄ Cl ₂ | | | | | (32.14) | (5.80) | (18.75) | (14.28) | (13.15) |
| 5. | [Co (L ²) ₂ (NO ₃) ₂] | Light | 65 | 285 | 500.93 | 28.58 | 5.20 | 22.50 | 31.85 | 11.56 |
| | CoC ₁₂ H ₂₆ N ₈ O ₁₀ | Pink | | | | (28.74) | (5.19) | (22.54) | (31.94) | (11.76) |
| 6. | [Co (L ²) ₂ (CH ₃ COO) ₂] | Light | 70 | 240 | 494.93 | 38.80 | 6.50 | 16.58 | 25.75 | 11.80 |
| | CoC ₁₆ H ₃₂ N ₆ O ₈ | | | | | (38.79) | (6.46) | (16.97) | (25.38) | (11.90) |
| 7. | [Co (L ³) ₂] Cl ₂ | Pink | 70 | 205 | 613.93 | 35.00 | 3.85 | 13.58 | 26.00 | 9.49 |
| | CoC ₁₈ H ₂₄ N ₆ O ₁₀ Cl ₂ | | | | | (35.18) | (3.90) | (13.68) | (26.06) | (9.59) |
| 8. | [Co (L ³) ₂ (NO ₃) ₂] | Light | 68 | 290 | 666.93 | 32.33 | 3.55 | 16.80 | 38.35 | 8.59 |
| | CoC ₁₈ H ₂₄ N ₈ O ₁₆ | Pink | | | | (32.38) | (3.59) | (16.79) | (38.38) | (8.83) |
| 9. | [Co (L ³) ₂] (CH ₃ COO) ₂ | Pink | 65 | 210 | 660.93 | 39.54 | 4.51 | 12.57 | 33.69 | 8.71 |
| | CoH ₂₂ N ₃₀ N ₆ O ₁₄ | | | | | (39.94) | (4.53) | (12.70) | (33.89) | (8.91) |
| 10. | [Co (L ⁴) ₂ Cl ₂] | Pink | 60 | 199 | 603.93 | 39.63 | 3.54 | 13.90 | 21.20 | 9.65 |
| | CoC ₂₀ H ₂₂ N ₆ O ₈ Cl ₂ | | | | | (39.73) | (3.64) | (13.90) | (21.19) | (9.75) |
| 11. | [Co (L ⁴) ₂ (CH ₃ COO) ₂] | Pink | 60 | 206 | 656.93 | 36.45 | 3.31 | 17.00 | 34.00 | 9.00 |
| | CoC ₂₄ H ₂₈ N ₆ O ₉ | | | | | (36.53) | (3.34) | (17.04) | (34.09) | (8.97) |
| 12. | [Co (L ⁴) ₂ (NO ₃) ₂] | Light | 63 | 222 | 650.93 | 44.20 | 4.15 | 17.00 | 34.00 | 9.00 |
| | CoC ₂₀ H ₂₂ N ₈ O ₁₄ | Pink | | | | (44.24) | (4.30) | (17.04) | (34.09) | (8.97) |

IR spectra of nitrate complexes :

IR spectra of the nitrate complexes bands corresponding to the coordinated nitrate group. The coordinated nitrate group show absorption at 1505-1475 (ν_1), 1325-1275 (ν_3), 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_3), 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 1570-1592 cm^{-1} ν (C=O) and 1672-1695 cm^{-1} ν (C=S). It indicates the unidentate nature. On the other hand acetato complex with ligand L^3 shows bands correspondent to free acetate group.

Magnetic 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 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 2. 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 susceptibilities and electronic spectra as discussed earlier.

Ligand field parameters :

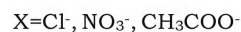
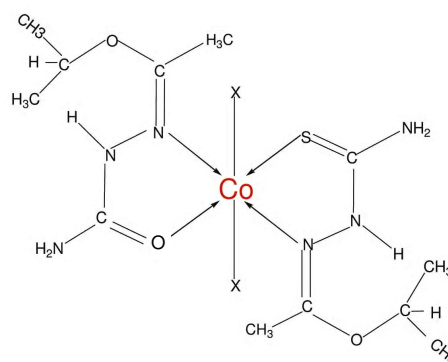
Various ligand field parameters viz., Dq, B, β and LFSE have been calculated and reported in Table 4. Dq values were evaluated by using Orgel diagram[35]. Nephelauxetic parameter β has been evaluated by using the equation.

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

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

Proposed structure of the complexes :

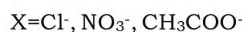
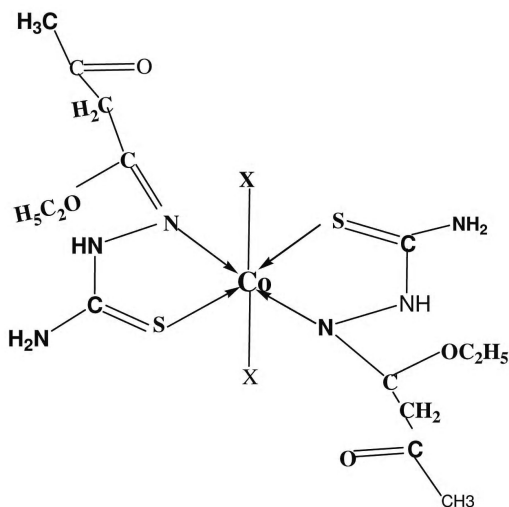
On the basis of elemental analysis, magnetic moment, molar conductance, IR, electronic and EPR spectral studies an octahedral geometry has been assigned for the complexes with ligand L^1 , L^2 , L^3 and L^4 as follows :



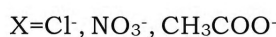
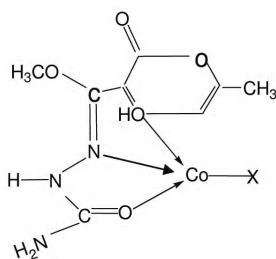
Cobalt complexes of isopropyl ester semicarbazone

Table 2 : Ligand field parameters and ESR spectral data of Co (II) complexes

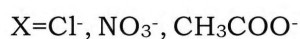
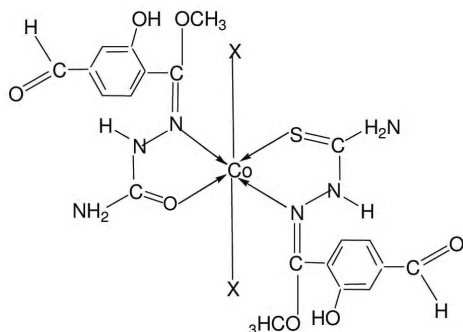
| Complex | Dq (cm^{-1}) | B (cm^{-1}) | β | LFSE KJ/mol^{-1} | g_{\parallel} | g_{\perp} |
|---|-------------------------|------------------------|---------|---------------------------|-----------------|-------------|
| $[\text{Co}(L^1)_2\text{Cl}_2]$ | 1291 | 717 | 0.64 | 124 | 3.62 | 2.32 |
| $[\text{Co}(L^1)_2(\text{NO}_3)_2]$ | 1401 | 778 | 0.70 | 134 | 3.99 | 2.27 |
| $[\text{Co}(L^1)_2(\text{CH}_3\text{COO})_2]$ | 1402 | 779 | 0.70 | 134 | 4.10 | 2.14 |
| $[\text{Co}(L^2)_2\text{Cl}_2]$ | 1339 | 744 | 0.66 | 128 | 4.93 | 2.41 |
| $[\text{Co}(L^2)_2(\text{NO}_3)_2]$ | 1269 | 705 | 0.63 | 121 | 4.13 | 2.15 |
| $[\text{Co}(L^2)_2(\text{CH}_3\text{COO})_2]$ | 1399 | 778 | 0.69 | 134 | 3.92 | 2.23 |
| $[\text{Co}(L^3)_2\text{Cl}_2]$ | 1385 | 770 | 0.69 | 133 | 3.96 | 2.21 |
| $[\text{Co}(L^3)_2(\text{NO}_3)_2]$ | 1291 | 717 | 0.64 | 124 | 4.85 | 2.16 |
| $[\text{Co}(L^3)_2(\text{CH}_3\text{COO})_2]$ | 1271 | 706 | 0.63 | 121 | 3.25 | 2.13 |
| $[\text{Co}(L^4)_2\text{Cl}_2]$ | 1295 | 720 | 0.64 | 124 | 4.27 | 2.32 |
| $[\text{Co}(L^4)_2(\text{NO}_3)_2]$ | 1300 | 723 | 0.65 | 124 | 4.76 | 2.17 |
| $[\text{Co}(L^4)_2(\text{CH}_3\text{COO})_2]$ | 1215 | 676 | 0.60 | 116 | 4.15 | 2.13 |



Cobalt complexes of acetoacetate ester semicarbazone



Cobalt complexes of Methyl ester of 6-methyl Pyran-2-one-4 hydroxy 3 diacarbonylic acid semicarbazone



Cobalt complexes of 3-Formylmethyl salicylate semicarbazone

Acknowledgement :

We are thankful to I.I.T. Delhi, I.I.T. Roorkee, Zakir Husain Delhi College, New Delhi, D.A.V. College, Muzaffarnagar for the laboratory facilities and also wants to thank U.G.C. for the financial assistance given while working as J.R.F..

Authors Affiliation :

DINESH KUMAR AND MRADULA MITTAL, Department of Chemistry, D.A.V. (P.G.) College, MUZAFFARNAGAR (U.P.) INDIA

REFERENCES

1. **Yogeeswari, P.**, Sriram, D., Suniljit, L.R.J., Kumar, S.S. and Stable, J.P. (2002). *Eur. J. Med. Chem.*, **37**, 231.
2. **Yogeeswari, P.**, Sriram, D., Saraswat, V., Ragaxendran, J.V., Kumar, M.M., Murugesan, S., Thirumurugan, R. and Stables, J.P. (2003). *Eur. J. Pharm. Sci.*, **20**, 341.
3. **Pandeya, S.N.**, Yogeeswari, P. and Stables, J.P. (2000). semicarbazone, *Eur. J. Med. Chem.*, **35**, 879.
4. **Lal, R.A.**, Kumar, A. and Chakarbory, A. (2001). *J. Chem.*, **40A**, 422.
5. **Saleh, A.A.**, Khalil, S.M.E., Eid Lal, M.F. and El-Ghamry, M.A. (2003). *J. Coord. Chem.*, **56**, 467.
6. **Hiqashi, Yiskinito**, Jitscuikia, Daisuke, Chayamab, Kazuaki and Masao (2006). **1**, 85.
7. **Kuznetsov, M.I.**, Dement Ev, A.I. and Zhornik, V.V. (2001). *J. Mol. Struct. (THEOCHEM)*, **571**, 45.
8. **Dimmock, J.R.**, Vashishtha, S.C. and Stable, J.P. (2000). *Med. Chem.*, **35**, 241.
9. **Klimova, T.**, Klimova, E.I., Mertinez, Garcia, Mendez, M., Stivalet, J.M. and Ramirez, L.R. (2001). *J. Organomet. Chem.*, **633**, 137.
10. **Kizilicikh, I.**, Ulkuseven, B., Dasedemir, Y. and Akkurt, B. (2004). *Synth. React. Inorg. Met. Org. Chem.*, **34**, 653.
11. **Chandra, S., Sangeetika and Rathi, A.**(2001). *J. Saudi Chem. Soc.*, **5**(2), 175.
12. **Raman, N.**, Kulandaisamy, A. and Thangaraja, C. (2004). *Synth. React. Inorg. Met. Org. Met. Chem.*, **34**, 1191.
13. **Raman, N.** and Ravichandran, S. (2005). *Synth. React. Inorg. Met. Org. and Nano Met. Chem.*, **35**, 439.
14. **Chandra, S.** and Kumar, R. (2004). *Transition Met. Chem.*, (3) 29, 269.
15. **Prasad, S.** and Srivastava, A. (2007). *Transition Met. Chem.*, **32**, 143.
16. **Chandra, S.** and Kumar, R. (2005). *Synth. React. Inorg. Met. Org and Nano. Metal Chem.*, **35**, 103.
17. **Chandra, S.** and Kumar, R. (2005). *Synth. React. Inorg. Met. Org and Nano. Metal Chem.*, **35**, 161.
18. **Kasuja, N.C.**, Sekind, K., Shimada, N.S., Ishikawa, M., Nomiya, K. (2001). *J. Inorg. Biochem.*, **84**, 55.

19. **Cardia, M.C.**, Begala, M., Delogu, A., Maccioni, E., Plumitallo, A. (2000). *Farmaco*, **55**, 93.
20. **Beym, J.H.** (1960). Mass Spectrometry and Its application to Organic Chemistry, Elsevier, Amsterdam.
21. **Mohan, J.** (2001). Organic Spectroscopy, in Principal and Applications", Narosa Publishing House, DELHI (INDIA).
22. (a) **Dyer, J.R.** (1987). Application of Absorption Spectroscopy of Organic Compounds Sixth, Georgia Institute of Technology.
(b) **Pedrido, R.**, Bermejo, M.R., Romero, M., Vazquez, M., Noya, A.M.G., Manerio, Rodriguez, M.J. and Fernandez, M.I. (2005). *Dalton Trans.*, 572.
23. **Tamboura, F.B.**, Haba, P.M., Gaye, M., Sall, A.S., Barry, A.H. and Jouini, T. (2004). *Polyhedron*, **23**, 1191.
24. **Chandra, S.** and Sharma, A.K. (2009). *Spectrochim Acta A.*, **72**, 651.
25. **Furniss, B.S.**, Hannaford, A.J., Smith, P.W.G. and Tatchell, A.R. (1989). Vogels Text Book Practical Organic Chemistry, eds, Longnan, London.
26. **Vogel, V.I.** (1962). Quantitative Inorganic Analysis, ELBS pp. 536-643.
27. **de Sousa, G.F.**, West, D.X., Brown, C.A., Swearingen, J.K., Valdes, J., Martines, Tascano, R.A., Hernandez-Ortega, S., Harner, M. and Bortoluzzi, A.J. (2000). *Polyhedron*, **19**, 841.
28. **Bonardi, A.**, Carini, C., Merlo, C., Pelizzi, C., Tarasioni, P. and Vitali, F. (1990). *J. Chem. Soc. Dalton Trans.*, 2771.
29. **Curtis, N.F.** (1964). *Inorg. Chem.*, **4** : 804.
30. **Gupta, L.K.**, Bansal, U. and Chandra, S. (2007). *Spectrochim. Acta A.*, **66**, 972.
31. **Ladeiro, C.**, Bastida, R., Bertolo, E. and Rodriguez, A. (2004). *Can. J. Chem.*, **82**, 437.
32. **Nakamoto, K.** (2004). Infrared and Spectra of Inorganic and Coordination Compounds, Third Ed., Wiley, Inter science, New York, **60**, 2153.
33. **Lever, A.B.P.** (1968). Elsevier, Amsterdam, p. 249.
34. **Lever, A.B.P.**, Lewis, J. and Nyholm, R.B. (1963). *J. Chem. Soc.*, **2552**.
35. **Beynn, J.H.** (1960). Mass Spectroscopy and its application to organic chemistry Elsevier, Amsterdam, NETHERLANDS.

