

Preparation and characterization of some addition complexes of cobalt(II) dithioacetylacetonate with Nitrogen donors

RENU SACHAR and SUVERCHA SHARMA*

Department of Chemistry, University of Jammu,
Babasaheb Ambedkar Road, Jammu - 180 006 (India)

(Received: May 17, 2008; Accepted: June 09, 2008)

ABSTRACT

A series of 1:1 addition complexes of Cobalt(II)dithioacetylacetonates with nitrogen donors such as morpholine, piperidine, piperazine, carbazole, dimethylamine, diethylamine and isopropylamine have been synthesized by treating the appropriate metal(II)dithioacetylacetonate with nitrogen donors in organic solvent. These addition complexes have been characterized by analytical data, electrical conductance, magnetic susceptibility measurements and electronic and infrared spectral studies. The biological activities of the complexes have also been carried out and they have been found to be antifungal in nature. NMR studies of some complexes has also been carried out.

Key words: Cobalt (II) dithioacetyl acetate, nitrogen donors.

INTRODUCTION

Dithioacetylacetonate moiety contains two thiocarbonyl groups in the place of carbonyl group of acetylacetonate ion. Their metal chelates have properties a little different from each other. These dithioacetylacetonate metal complexes of the anion (SacSac) have been synthesized by template or ligand trapping reactions of acetylacetonate and elegant metal ions in presence of ethanolic HCl with hydrogen sulphide at 0°C¹.

Dithioacetylacetonate complexes of many bivalent [M^{II} = Ni, Zn, Cd, Hg, Pd, Pt] and trivalent [M^{III} = Co, Rh, Ir, Ru, Fe, Os and Cr] transition metals have been synthesized and have been the subject of detailed physico-chemical studies. Physical measurements and structure determinations reveal that dithioacetylacetonate invariably behaves as bidentate chelating ligand via sulfur atoms, forming the complexes in which substantial electron delocalization takes place².

These dithioacetylacetonate complexes of transition metal ions have been used extensively in the analytical chemistry as pesticides, fungicides, vulcanization accelerators, floatation agents and good antioxidants for polyolefins e.g. Co(SacSac)₂ is a good oxidation inhibitor³. Ni(SacSac)₂ has also been used as antioxidants and vulcanization accelerators for polydienes and appear to be biomimetic for number of reactions observed for Nickel enzymes⁴. Though a lot of work on dithioacetylacetonate complexes of transition metal ions has been reported but not much work has been done on the additional complexes of Co(II)dithioacetylacetonate. This prompted us to prepare and investigate the additional complexes of Co(II)dithioacetylacetonate with nitrogen donors. The present communication reports the preparation and characterization of their addition complexes with nitrogen donors such as morpholine, piperidine, piperazine, carbazole, dimethylamine, diethylamine and isopropylamine.

EXPERIMENTAL

Preparation of Cobalt(II)dithioacetylacetonate complexes

Cobalt carbonate 3.0 (g) was dissolved in 10% w/w ethanolic hydrogen chloride (80mL) and the solution was cooled to 0°C. Acetylacetonate (10mL) was added and hydrogen sulphide was bubbled vigorously through the solution for about 2 hours. At the end of this time the color had changed from deep blue to deep green and some dark crystals had separated. The solution was allowed to come to room temperature and was left to stand for about 15 hours with gentle flow of hydrogen sulphide passing through it. The dark violet needle like crystals which had separated at the end of this time were filtered off and washed with ethanol until the washings were colorless. They were dried at the vacuum. The deep violet crystals obtained were soluble in organic solvents e.g. Chloroform, acetone, benzene but insoluble in water and alcohol. The compound did not melt and decomposed at about 180°C (5).

Preparation of the addition complexes of Co(II)dithioacetylacetonate with nitrogen donors

The addition complexes of $\text{Co}(\text{SacSac})_2$ were prepared by the interaction of $\text{Co}(\text{SacSac})_2$ (1.604 g, 0.005 mol) in acetone (120mL) with nitrogen donors [morpholine = 0.484mL, piperazine = 0.430g, piperidine = 0.532mL, carbazole = 0.836g, diethylamine = 0.365mL, dimethylamine = 0.281mL, isopropylamine = 0.430mL (0.005 mol)] and stirred for half an hour under nitrogen atmosphere to prevent oxidation of Co(II) to Co(III). The reaction mixture was then refluxed gently under nitrogen atmosphere for 3-4 hours and allowed to stand for 20-24 hours. On standing, the addition complexes formed were washed several times with the solvent used in their preparation and dried in vacuum.

METHODS

Carbon, Hydrogen, Nitrogen and Sulfur were determined on Elemental analyzers (Elementar Vario EL III, Carlo Erba 1108). Molar conductance was determined on the millimolar solution in DMF using (Centuary CC60 Conductivity Bridge). Electronic spectra were recorded on

Table 1: Analytical and Molar Conductance of data of adducts of Cobalt(II)dithioacetylacetonate with nitrogen donors

S. no.	Adducts	Formula	%age found				%age calculated				Molar conductance ($\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$)
			C	H	N	S	C	H	N	S	
1.	$\text{Co}(\text{SacSac})_2$ morpholine	$\text{C}_{14}\text{H}_{23}\text{ONS}_4\text{Co}$	41.18	5.63	3.43	31.37	41.10	5.56	3.43	31.31	0.44
2.	$\text{Co}(\text{SacSac})_2$ piperidine	$\text{C}_{15}\text{H}_{25}\text{NS}_4\text{Co}$	44.34	6.15	3.44	31.53	44.28	6.10	3.36	31.44	0.62
3.	$\text{Co}(\text{SacSac})_2$ piperazine	$\text{C}_{14}\text{H}_{24}\text{N}_2\text{S}_4\text{Co}$	41.28	5.89	6.88	31.45	41.18	5.80	6.79	31.39	0.94
4.	$\text{Co}(\text{SacSac})_2$ carbazole	$\text{C}_{22}\text{H}_{23}\text{NS}_4\text{Co}$	54.10	4.71	2.86	26.23	54.06	4.65	2.79	26.17	0.76
5.	$\text{Co}(\text{SacSac})_2$ diethylamine	$\text{C}_{12}\text{H}_{21}\text{NS}_4\text{Co}$	39.35	5.73	3.82	32.97	39.30	5.69	3.75	34.89	0.40
6.	$\text{Co}(\text{SacSac})_2$ dimethylamine	$\text{C}_{14}\text{H}_{25}\text{NS}_4\text{Co}$	42.64	6.34	3.55	32.49	42.61	6.31	3.52	32.44	0.36
7.	$\text{Co}(\text{SacSac})_2$ isopropylamine	$\text{C}_{13}\text{H}_{23}\text{NS}_4\text{Co}$	41.05	6.05	3.68	33.68	41.01	5.59	3.60	33.59	0.87

(JascoV513spectrophotometer). Infra-red spectra of the complexes over the region 4000-400 cm^{-1} were recorded using KBr pellets on Infrared spectrometer(Perkin Elemer FT- IR spectrometer) . Magnetic moments were determined at room temperature by VSM method (Princeton Applied

Research- Model no.155). Analytical data and the molar conductance of adducts prepared are presented in the Table 1. Magnetic moments, important electronic and infrared bands are cited in Table 2.

Table 2: Magnetic and spectral data of adducts of Cobalt(II) dithioacetylacetonate with nitrogen donors

S. no.	Adducts	Electronic spectra			Magnetic Momentin B.M.at 294 K	IR spectra		
		ν_1	ν_2	ν_3		$\nu(\text{C-C})$	$\nu(\text{C-S})$	$\nu(\text{N-H})$
1.	Co(SacSac) ₂ morpholine	18120	27650	32950	2.52	1490.6	749.8	3342
2.	Co(SacSac) ₂ piperidine	18350	28210	33450	2.71	1487.4	748.3	3295
3.	Co(SacSac) ₂ piperazine	18710	28450	34510	2.22	1490.5	745.5	3239
4.	Co(SacSac) ₂ carbazole	18984	29150	35100	2.66	1491.1	748.3	3386
5.	Co(SacSac) ₂ diethylamine	18220	27550	32850	2.14	1490.6	749.8	3210
6.	Co(SacSac) ₂ dimethylamine	18320	28310	33550	2.28	1487.4	748.3	3189
7.	Co(SacSac) ₂ isopropylamine	18510	29450	34410	2.34	1490.5	745.4	3201

RESULTS AND DISSUSION

The adducts of Co(II) dithioacetylacetonate are microcrystalline solids. The adducts of Co(II)dithioacetylacetonate are blackish-green in color All these are stable to air and moisture and soluble in many organic solvents such as chloroform, benzene, acetone etc. giving intensely colored stable solutions. On the basis of their elemental analysis (CHNS), the addition complexes have been assigned the general formula $M(\text{SacSac})_2\text{L}$ [$M = \text{Co(II)}$; SacSac = dithioacetylacetonate anion ; L= morpholine, piperidine, piperazine, carbazole dimethylamine, diethylamine and isopropylamine] which shows that they are of 1:1 stoichiometry^{6,7}. Conductance values of these complexes in DMF fall in the range 0.36-

0.94 $\text{mole}^{-1}\text{ohm}^{-1}\text{cm}^2$ (Table 1). These values are far less than the values of 120-140 $\text{mole}^{-1}\text{ohm}^{-1}\text{cm}^2$ reported for uni-univalent electrolytes in this solvent, which suggests a non-conducting nature of these complexes⁸. The magnetic moment values of 1:1 addition complexes of Cobalt(II) dithioacetylacetonate fall in the range of 2.14-2.71 B.M. supports the argument that SacSac as ligand is of high field strength and give rise to low-spin Co(II) complexes in which it adopts a square-pyramidal geometry having one unpaired electron .The observed magnetic moment value is greater than spin only magnetic moment value showing that there is an appreciable orbital contribution⁹ (Table 2). Electronic spectra of the addition complexes of Co(II)dithioacetylacetonate have been recorded in the range 13500-35800 cm^{-1} .

Electronic spectra of Cobalt(II)dithioacetylacetonate complexes shows three bands in the range 18000-19200 cm^{-1} , 27500-29004 cm^{-1} and 32000-35800 cm^{-1} designated as ν_1 , ν_2 and ν_3 , which are similar to square pyramidal Cobalt(II)complexes (10) (Table 2). A comparison of Infrared spectra of the present complexes with those of the free ligand reveals that most of the absorption bands of free ligands shifted in their respective complexes. These addition complexes show a sharp band in the higher frequency region of 1497-1520 cm^{-1} indicating positive shift as compare to the bands of parent Co(II) dithioacetylacetonate, which confirm the bonding of ligand to the metal ion through amine

group [11] (Table-2). ^1H NMR of $\text{Co}(\text{SacSac})_2$ morpholine(CDCl_3) δ : 2.3(due to aliphatic C-H stretching of the methyl group), 2.5(CH_2 of morpholine), 3.0(NH of morpholine), 7.1(aromatic C-H stretching). The invitro biological screening effects of the novel investigated addition complexes of Co(II)dithioacetylacetonate were tested against fungus-'*Fusarium moniliforme*' and '*Aspergillus niger*'. It is concluded that these novel investigated addition complexes of Co(II)dithioacetylacetonate exhibit higher antifungal activity than $\text{Co}(\text{SacSac})_2$ and free ligand, but lower activity than that of standard drug.

REFERENCES

1. Lockyer T.N, and Martin R.L, Progress in *Inorganic Chemistry.*, **27**: 224 (1980).
2. Heath G.A and Leslie J.H, *J. Chem. Soc. Dalton Trans*, 1587 (1983).
3. Karshaykov K (Inst.Org.Chem, Sofia, Bulg) Dokl. Bolg.Akad.Nauk, **39**: 3969-72 (1986).
4. Kishore K, Verneker Pai V.R , Dharamraj G.Varghese, *J.Polym.Sci, Polym, Lett Ed.* **21**: 627-31 (1983).
5. Barraclogh C.G, Martin R.L. and Stewart I. M, *Aust. J.Chem*, **22**: 891(1969).
6. Darensbourg, D.J, Adams, M. J. and Yarbrough, J.C, *Inorganic Chemistry Communication*, **5**: 38 (2002).
7. Ives C, Fillis E.L. and Hagadorn J. R, *Dalton Trans*, **4**: 527 (2003).
8. Martin R.L. and Whitley A., *J. Chem. Soc.*, 1394 (1958).
9. Sankhla D.S, Arora O.P. and Misra S.N., *Ind. Jour. Chem*, **17A**: 610 (1979).
10. Simman O. and Fresco J, *Journal of the American Chemical Society*, 2652 (1969).
11. Bertini I, Dapporto P, Gateschi D. and Scozzafare, A, *Inorg. Chem.*, **14**: 1639 (1975).