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SYNTHESIS AND CHARACTERIZATION OF SOME TRINUCLEAR COBALT(II) THIOCARBO XYLATES

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY Vol. 32, No. 10, pp. 1855–1864, 2002

SYNTHESIS AND CHARACTERIZATION OF SOME TRINUCLEAR COBALT(II) THIOCARBOXYLATES

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ABSTRACT

Some cobalt(II) complexes of thiocarboxylic acids with the general composition $Co(SOCR')_2$ and Co(SOCR')(OOCR)[where $R = C_{13}H_{27}$, $C_{15}H_{31}$ or $C_{17}H_{35}$ and $R' = CH_3$ or C_6H_5] have been synthesized by substitution reactions and characterized by elemental analyses, spectral studies and magnetic moment measurements. The electrical conductance data indicate that ($Co(SOCCH_3)_2$ is a 1:2 electrolyte while the other complexes are non-electrolytes. IR spectra show the presence of bidentate and bridging modes of coordination for carboxylate and thiocarboxylate anions, respectively. Electronic spectral data and magnetic moment values indicate an octahedral environment around cobalt(II). The plausible structure for the trimeric species has been proposed on the basis of the

1855

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physico-chemical studies. Thermoanalytical data indicate the complexes are stable upto 175 $^{\circ}\mathrm{C},$ above which decomposition starts.

INTRODUCTION

Thiocarboxylic acids and their transition metal complexes recently^[1-3] have attracted attention not only because they contain both 'soft' sulfur and 'hard' oxygen donor sites, but also because of their wide variety of technological applications.^[4,5] A perusal of the literature reveals that thiocarboxylato complexes of nickel, palladium, copper, zinc, silver, cadmium, and mercury^[6–8] have been studied in view of the fact that these compounds are widely used as homogeneous catalysts in many reactions like hydrogenation, hydrogen transfer, isomerization, hydrosilylation, carbonylation and hydroformylation. However, it appears that very limited attention has been paid to similar derivatives of iron and cobalt.^[9,10] The literature also reveals that no complex of cobalt(II) has been reported in which one ligand is a simple carboxylic acid and the other one is a thiocarboxylic acid.

In view of the above objectives, the present work has been carried out to synthesize some *bis*(thiocarboxylato) and mono(carboxylato)mono(thiocarboxylato) complexes of cobalt(II) by stepwise substitution reactions. This method is a convenient route to synthesize these complexes. The complexes have been characterized by physico-chemical methods and the coordination behaviour of carboxylate and thicarboxylate anions towards cobalt(II) was explored. Molecular weights of the complexes were determined and their plausible structure has been suggested on the basis of these studies.

RESULTS AND DISCUSSION

Synthesis of Cobalt(II) Complexes

The following substitution reactions of cobalt(II) acetate or thioacetate with carboxylic acids or thiocarboxylic acids were carried out in toluene under reflux (Table I).

$$Co(OOCCH_3)_2 + 2R'COSH \rightarrow Co(SOCR')_2 + 2CH_3COOH \uparrow (1)$$

TRINUCLEAR COBALT(II) THIOCARBOXYLATES

	Table I.	Analytical Data of Thioc	carboxylato Com	plexes of Col	oalt(II)				
					Analysis	, Found	(Calcd.)		
	Reactants	Product	Empirical Formula (Melting/Decom.	CH ₃ COSH/ CH ₃ COOH	C	C	Н	s	Mol.
S. No.	(g, mmol)	(Colour, Yield in %)	Point in °C)	(g)	(%)	(%)	(%)	(%)	Wt.
E	$C_0(OOCCH_3)_2 + CH_3COSH$ (6.56, 37.0) + (5.64, 74.0)	Co(SOCCH ₃) ₂ (Brownish black, 78)	C ₄ H ₆ CoO ₂ S ₂ (138)	I	28.14 (28.19)	22.92 (22.98)	2.91 (2.90)	30.69 (30.67)	_ (209)
3	Co(SOCCH ₃) ₂ + C ₁₃ H ₂₇ COOH (2.23, 10.7) + (2.43, 10.7)	Co(SOCCH ₃)(OOCC ₁₃ H ₂₇) (Brownish red, 61)	C ₁₆ H ₃₀ CoO ₃ S (117)	0.80 (0.81)	16.27 (16.30)	53.14 (53.17)	8.36 (8.38)	8.82 (8.87)	- (361)
(3)	$\begin{array}{l} Co(SOCCH_3)_2+C_{15}H_{31}COOH\\ (2.16,\ 10.3)+(2.65,\ 10.3)\end{array}$	Co(SOCCH ₃)(OOCC ₁₅ H ₃₁) (Brownish red, 57)	C ₁₈ H ₃₄ CoO ₃ S (121)	0.80 (0.79)	15.09 (15.13)	55.47 (55.51)	8.79 (8.82)	8.18 (8.23)	1180 (389)
(4)	$\begin{array}{l} Co(SOCCH_3)_2+C_{17}H_{35}COOH\\ (2.68,\ 12.8)+(3.65,\ 12.8)\end{array}$	Co(SOCCH ₃)(OOCC ₁₇ H ₃₅) (Brownish red, 55)	C ₂₀ H ₃₈ CoO ₃ S (127)	0.97 (0.98)	14.09 (14.12)	<i>57.57</i> (<i>5</i> 7.53)	9.18 (9.19)	7.62 (7.68)	1272 (417)
(2)	$\begin{array}{c} C_{0}(OOCCH_{3})(OOCC_{13}H_{27}) + \\ C_{6}H_{5}COSH \\ C_{7} = 0 & 0.1 & 1.10 & 0.0 \end{array}$	Co(SOCC ₆ H ₅)(OOCC ₁₃ H ₂₇)	C ₂₁ H ₃₂ CoO ₃ S	0.47	13.94	59.56 (50.55)	7.53	7.53	1296
(9)	(2. /6, 8.0) + (1.10, 8.0) Co(OOCCH ₃)(OOCC ₁₅ H ₃₁) + C ₆ H ₅ COSH	(<i>U</i> ark brown, <i>9</i>) Co(SOCC ₆ H ₅)(OOCC ₁₅ H ₃₁)	(179 d) C ₂₃ H ₃₆ CoO ₃ S	(0.48) 0.43	(13.91) 13.04	(cc.୧c) 61.18	(0C./) 7.99	(/ <i>C.</i> /) 99.9	(424) -
	(2.52, 6.7) + (0.93, 6.7)	(Brownish red, 58)	(182 d)	(0.41)	(13.06)	(61.21)	(2.98)	(7.10)	(451)
Ð	Co(OOCCH ₃)(OOCC ₁₇ H ₃₅) + C ₆ H ₅ COSH	Co(SOCC ₆ H ₅)(OOCC ₁₇ H ₃₅)	$C_{25}H_{40}CoO_3S$	0.35	12.26	62.53	8.32	6.67	1466
	(2.37, 5.9) + (0.82, 5.9)	(Redish brown, 56)	(181 d)	(0.35)	(12.28)	(62.58)	(8.34)	(6.68)	(480)
(8)	$\begin{array}{l} Co(OOCCH_3)_2+C_6H_5COSH\\ (2.64,14.9)+(4.12,29.8)\end{array}$	Co(SOCC ₆ H ₅) ₂ (Brick red, 82)	C ₁₄ H ₁₀ CoO ₂ S ₂ (187 d)	1.77 (1.79)	17.64 (17.68)	50.43 (50.45)	2.97 (3.00)	19.24 (19.24)	1008 (334)

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1857

$$Co(SOCCH_3)_2 + RCOOH \rightarrow Co(SOCCH_3)(OOCR) + CH_3COSH \uparrow$$
(2)

$$Co(OOCCH_3)_2 + RCOOH \rightarrow Co(OOCCH_3)(OOCR) + CH_3COOH \uparrow$$
(3)

$$\begin{array}{l} Co(OOCCH_3)(OOCR) + C_6H_5COSH \ \rightarrow \ Co(SOCC_6H_5)(OOCR) \\ + CH_3COOSH \uparrow \end{array} \tag{4}$$

where $R = C_{13}H_{27}$, $C_{15}H_{31}$ or $C_{17}H_{35}$ and $R' = CH_3$ or C_6H_5 .

All of these reactions were facile and their progress could be followed by determining the acetic acid or thioacetic acid content in the collected azeotrope. The synthesized complexes are non-volatile, coloured solids which could be recrystallized or reprecipitated. The measured molar conductances of the mono(carboxylato)mono(thiocarboxylato)cobalt(II) complexes at 10^{-2} – 10^{-4} molar concentrations in nitrobenzene were found to be in the range 0.8-9.3 ohm⁻¹ cm² mol⁻¹. These values indicate their nonelectrolytic nature. Thermogravimetric analyses of the complexes were done in the temperature range 30–600 °C and the results indicate the complexes are stable up to 175 °C. Below this temperature, there was hardly any weight loss in the samples. The decomposition started above 180 °C and there was a gradual loss up to 600 °C where the percentage loss was observed to be about 75%.

IR Spectra

In the infrared spectra of thiocarboxylic acids, the v(S-H) band appears in the region 2600–2550 cm⁻¹. This band was completely missing in the spectra of the complexes indicating deprotonation of thiocarboxylic acids. Similarly, the O–H stretching vibrations of carboxylic acids (in the region 3600–3300 cm⁻¹) were absent in the complexes, which indicates deprotonation of the carboxylic acids. The characteristic vibrations of v(C=O) and $\delta(O-H)$ of free carboxylic acids which appear at 1700 and 935 cm⁻¹, respectively, were found absent in the infrared spectra of the complexes. This indicates that carbonyl oxygen of the COO or COS group is coordinated to the metal which can occur in any one of the following types shown in Fig. 1.

TRINUCLEAR COBALT(II) THIOCARBOXYLATES



1859

Figure 1. Various coordination modes of thiocarboxylate anion.

Although detailed infrared spectral studies have been carried out to distinguish the modes of coordination of carboxylate and thiocarboxylate anions,^[11] no sharp line seems to be available to categorize these on the basis of C=O and C=S stretching frequencies. However, a comparison of these frequencies observed in the complexes with those of the sodium salt can be helpful in distinguishing the type of bonding between cobalt(II) and the carboxylate or thiocarboxylate ion. The positions of $v_{asym}(C=O)$ and $v_{asym}(C=O)$ of the carboxylate ion in the complexes, observed at 1567 and 1465 cm⁻¹, respectively, and shift in the v(C=S) frequency from 755 to 722 cm⁻¹ suggest the bonding is of type I (bridging mode of coordination in Fig. 1) in the complexes. The behavior of carboxylate and thiocarboxylate anions in the complexes is, therefore, bidentate as well as bridging involving the coordination of both oxygen and sulfur atoms of the ligands. The bands observed at ~500 and ~400 cm⁻¹ may be due to Co–O and Co–S vibrations, respectively.^[11]

Electronic Spectra and Magnetic Moments

Six-coordinate octahedral cobalt(II) complexes exhibit three spinallowed bands in the electronic spectra which can be assigned to ${}^{4}T_{2g}(F) \leftarrow {}^{4}T_{1g}(F), {}^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$ and ${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)$ transitions. These are known to occur at 7500–10,000 (v₁), 12,000–17,000 (v₂) and 19,000–23,000 (v₃) cm⁻¹, respectively.^[12] The electronic spectra of the complexes exhibited three bands and their positions (Table II) indicate a pseudo-octahedral geometry around cobalt(II). The ligand field splitting energy (10Dq), interelectronic repulsion parameter (B) and covalency factor (β) have been calculated using the secular equations given by Underhill and Billing.^[13]

$$340Dq^2 + 18(\upsilon_3 - 2\upsilon_2)Dq + \upsilon_2^2 - \upsilon_2 \cdot \upsilon_3 = 0$$
(5)

$$B = \{(v_3 - 2v_2) + 30Dq\}/15 \tag{6}$$

		0	Observed Transitions	0_				
S.No.	Compounds ^b	$ {}^{4}T_{2g}(F) \leftarrow {}^{4}T_{1g}(F) $ $ (\upsilon_{1}) $	${}^{4}\mathrm{A}_{2g}(F) \! ^{4}\! T_{1g}(F) \\ (\upsilon_{2})$	$\label{eq:states} \begin{split} {}^{4}\! T_{1g}(P) \! \leftarrow^{4}\! T_{1g}(F) \\ (\upsilon_3) \end{split}$	10 Dq	В	β	$_{(B.M.)}^{\mu_{eff}}$
E	Co(SOCCH ₃) ₂	8,232	16,330	22,650	8763	1085	0.97	5.18
5	$C_0(SOCCH_3)(OOCC_{13}H_{27})$	8,188	16,382	20,000	8750	899	0.80	4.91
(E)	$C_0(SOCCH_3)(OOCC_{15}H_{31})$	8,204	16,438	19,726	8774	878	0.78	4.96
(4)	Co(SOCCH ₃)(OOCC ₁₇ H ₃₅)	8,126	16,182	19,430	8637	865	0.77	4.87
(2)	$C_0(SOCC_6H_5)(OOCC_{13}H_{27})$	7,957	16,342	19,250	8716	848	0.76	5.02
9	Co(SOCC ₆ H ₅)(OOCC ₁₅ H ₃₁)	8,143	16,503	19,796	8808	881	0.79	4.89
6	Co(SOCC ₆ H ₅)(OOCC ₁₇ H ₃₅)	8,116	16,474	19,930	8796	891	0.80	4.83
(8)	Co(SOCC ₆ H ₅) ₂	8,196	16,349	20,247	8737	917	0.82	5.16
^a Electr ^b (1) in	onic transitions, 10Dq and B an methanol and (2) to (8) in tolue	e in cm ⁻¹ . sne.						
^c ε valu	es in L mol ⁻¹ cm ⁻¹ (for $v_1 = 2$ -	5; $v_2 = 10 - 15$ and v_3	= 30 - 35).					

Complexes of Cobalt(II)
of Thiocarboxylato
Moments
Magnetic
and
Electronic Spectra ^a
Table II.

BARANWAL AND GUPTA

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1860

TRINUCLEAR COBALT(II) THIOCARBOXYLATES

The values of the interelectronic repulsion parameter are found to be below the free-ion value for Co(II) ion (1120 cm⁻¹) and show a considerable covalent nature of the metal-ligand bond in all of the complexes except in bis(thioacetato)cobalt(II). The B and β values for this compound were found to be 1085 cm⁻¹ and 0.97, respectively, which suggested its ionic nature. Magnetic moments of the complexes, measured at the room temperature, were in the range 4.83–5.18 BM. This is typical for cobalt(II) complexes (d⁷ system) in octahedral geometry^[14] due to orbital contribution.

Molecular Weights and Probable Structure

Molecular weights of some representative complexes were determined by the cryoscopic method in benzene and the results (Table I) suggested that all of the complexes are trimeric. On the basis of the findings from the infrared and electronic spectra of the complexes, their plausible structure is proposed in Fig. 2 in which cobalt(II) is situated in an octahedral environment. Many other cobalt(II) complexes have been reported to have a similar structure.^[15,16] Attempts are being made to grow single crystals suitable for structure determination.

EXPERIMENTAL

All the reactions were carried out under anhydrous conditions. Cobalt(II) acetate tetrahydrate was made anhydrous by refluxing in an



Figure 2. Proposed structure for trimeric cobalt(II) complexes.

excess of acetic anhydride (2 h) and drying *in vacuo*. Toluene and benzene were distilled over sodium. The carboxylic acids were used after distillation under reduced pressure (m.p. of myristic acid: 58 °C, palmitic acid: 63 °C and stearic acid: 70 °C). Thioacetic acid (Fluka, purum) and thiobenzoic acid (Fluka, pract) were distilled before use. Cobalt was determined as $Co[Hg(SCN)_4]$.^[17] The liberated acetic and thioacetic acids in the collected azeotrope were determined by titration with standard sodium hydroxide solution using phenolphthalein as indicator. Sulfur was determined as barium sulfate.^[18] IR spectra were recorded on a model 125 Perkin-Elmer spectrophotometer using KBr discs. Other physico-chemical studies were carried out as given in earlier publications.^[19,20]

Synthesis of *bis*(Thioacetato)cobalt(II)

Thioacetic acid (5.64 g, 74.0 mmol) was added slowly to a toluene (100 mL) suspension of $Co(OOCCH_3)_2$ (6.56 g, 37.0 mmol) with constant stirring. The colour of the reaction mixture changed from violet to brownish black. The contents were refluxed for 5 h and the insoluble product was filtered, washed with toluene and finally dried *in vacuo*. A brownish black solid was obtained. This solid was reprecipitated from its methanolic solution by adding an excess of benzene and dried *in vacuo*.

Synthesis of Mono(myristato)mono(thioacetato)cobalt(II)

Myristic acid (2.43 g, 10.7 mmol) was dissolved in 50 mL toluene. This solution was added slowly to a toluene (50 mL) suspension of $Co(SOCCH_3)_2$ (2.33 g, 10.7 mmol) with constant stirring. The colour of the reaction mixture changed from brownish black to brownish red. The contents were refluxed for 8–10 h with slow and continuous azeotropic fractionation of the liberated thioacetic acid with toluene (b.p. 103 °C). The product was soluble in toluene. The excess solvent was removed *in vacuo* to yield a brownish red solid. This solid was soluble in benzene and insoluble in ethyl alcohol. The product was reprecipitated from its benzene solution by adding an excess of ethanol. The precipitate was finally dried *in vacuo*. The same procedure was adopted for synthesis of the other complexes of cobalt(II), (3) and (4).

Synthesis of Mono(palmitato)mono(thiobenzoato)cobalt(II)

Palmitic acid (4.34 g, 16.9 mmol) was added to a toluene (100 mL) suspension of $Co(OOCCH_3)_2$ (2.99 g, 16.9 mmol). The contents were

refluxed for 10–12 h with slow and continuous azeotropic fractionation of the liberated acetic acid with toluene (b.p. 106 °C). The product was soluble in toluene. The excess solvent was removed *in vacuo* giving a violet solid. To this monosubstituted product (2.52 g, 6.7 mmol), dissolved in toluene (100 mL), thiobenzoic acid (0.93 g, 6.7 mmol) was added. The mixture was refluxed for 12 h and the acetic acid-toluene azeotrope was removed slowly by fractional distillation. The excess solvent was removed *in vacuo* to yield a brownish red solid. This was reprecipitated from its benzene solution by the addition of ethanol. The other complexes of cobalt(II) (5), (7) and (8) were prepared following the same procedure.

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