ADDITION COMPLEXES OF Co(II) ARYL CARBOXYLATES WITH PYRIDINES

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(First received 16 January 1979; received for publication 8 November 1979)

Abstract—A large number of complexes of pyridine ligands have been prepared with different Co(II) aryl carboxylates $Co(O_2CC_6H_4R)_2$ (where R is H, CH₃-o, Cl-o and m, NO₂-o and m, CH₃O-m). Pyridine (Py), 3-and 4-Methyl Pyridine (3- and 4-MePy) yield *bis-amine* complexes of 1:2 stoichiometry $Co(O_2CC_6H_4R)_2L_2$ which have been shown by magnetic and spectral studies to possess a *trans* octahedral configuration. By contrast, 2-Methyl Pyridine (2-MePy) yields 1:1 complexes which are considered to be monomeric, five coordinate trigonal bipyramidal molecules except that of cobalt(o-toluate)₂ complex which is a dimeric syn–syn carboxylate bridged species.

INTRODUCTION

A general survey of literature on complexes of Co(II) with nitrogen donors reveals that although a considerable amount of work has been carried out on the preparation and characterisation of addition complexes of Co(II) carboxylates with nitrogen donors yet there are many gaps left in the development of their chemistry. For instance, there was no reference available in literature on the preparation and characterisation of adducts of Co(II) aryl carboxylates with heterocyclic nitrogen donors when the present study was undertaken. However, during the course of this investigation some adducts of Co(II) benzoate [1, 2] and nitrobenzoate [2] appeared with pyridine, 2-methyl pyridine and quinoline.

Further, carboxylates of divalent metals are noted to give with various donor ligands complexes of three different stoichiometries [3-7], viz. 1:1, 1:2 and 1:4. In some cases a metal carboxylate may give adducts of two different stoichiometries with the same ligand under different experimental conditions [8, 9]. The preparation of the adducts of Co(II) aryl carboxylates was undertaken with a view to investigating the nature of the addition complexes obtained and to examine whether the adducts of 1:1 stoichiometry obtained herein possess dinuclear carboxylate bridged structure and sub-normal magnetic moments similar to the 1:1 complexes of Cu(II) carboxylates with pyridine and other bases. A few complexes reported earlier by some other group[2] have also been included here because we have obtained them independently by a slightly different procedure.

EXPERIMENTAL

Methods and materials. Basic cobalt carbonate 2CoCO₃. 3Co(OH)₂(B. D. H.) was purified by repeated washings with hot water to dissolve any soluble impurity and drying in air. Purity of carboxylic acids (B. D. H.) used was established by checking their sharp melting points after recrystallisation from hot water or benzene or ethanol. Heterocyclic ligands were fractionally distilled after keeping them over potassium hydroxide pellets over night. Solvents were purified by conventional methods [10].

Cobalt was estimated gravimetrically as tetrapyridine dithiocyanato Co(II). Carbon and hydrogen were determined in the micro-analytical laboratory of this department. Molar conductance was determined on millimolar solutions in methanol using a Toshniwal conductivity bridge type CLO/0.2 A. Molecular weights were determined cryoscopically in nitrobenzene. Magnetic moments were determined by Gouy's method. Electronic spectra were scanned on Beckman-DB-Spectrophotometer and Beckman-Du-2-Spectrophotometer in methanol or benzene. Diffuse reflectance spectra were recorded on Carl-Zeiss DMR-21 UV visible spectrophotometer. IR spectra were recorded on Perkin-Elmer double beam spectrophotometer Model 621 as Nujol or hexachlorobutadiene mulls in sodium chloride plates or in polyethylene sheets.

Preparation of the complexes. Adducts were prepared by the addition of the heterocyclic amine in 1:1 or 1:2 metal to ligand ratio to the fresh Co(II) aryl carboxylate generated in ethanolic solution by refluxing a solution of the appropriate aryl carboxylic acid in ethanol with basic cobalt carbonate for 14-48 hr depending upon the strength of the particular carboxylic acid. The reaction mixture on filtration and subsequent work up invariably gave a crystalline product which was separated, recrystallised from methanol or any other suitable solvent and dried in vacuum over phosphorus pentoxide at room temperature. Procedures for pyridine complexes are given below:

Bis(benzoato)bis(pyridine)Co(II). Basic cobalt carbonate (1.29g; 0.0025 mole) in slight excess than required was treated with benzoic acid (2.44g; 0.02 mole) in methanol (120 ml) in a 250 ml round-bottomed flask fitted with a reflux condenser connected to a calcium chloride guard tube. The contents of the flask were refluxed on a water-bath for about 48 hr. The excess of the carbonate was filtered off and two equivalents of pyridine (1.58g; 0.02 mole) were added to the filtrate. The resulting deep red solution on removal of the solvent under reduced pressure deposited reddish pink crystals of $Co(O_2CC_6H_5)_2.2C_5H_5N$, which were separated, recrystallised from ethanol and finally dried in vacuum over phosphorus pentoxide at room temperature (Yield 2.07g, 45.2%).

Bis(o-toluato)bis(pyridine)Co(II). To a solution of o-toluic acid (2.72g; 0.02 mole) in ethanol (130 ml) cobalt carbonate (1.29g; 0.0025 mole) was added and the reaction mixture was heated for 35 hr under reflux. After filtration two equivalents of pyridine (1.58g; 0.02 mole) were added. The reaction mixture on concentration gave reddish pink crystals of Co($O_2CC_6H_4CH_3$ $o_{12}.2C_5H_5N$, which were recrystallised from methanol and dried as described above (Yield 3.20g; 64.2%).

Bis(o-chlorobenzoato)bis(pyridine)Co(II). Cobalt carbonate (1.29g; 0.0025 mole) was heated under reflux for 30 hr with o-chlorobenzoic acid (3.13g; 0.02 mole) dissolved in ethanol (125 ml). It was filtered and two equivalents of pyridine (1.58g; 0.02 mole) were added to the filtered solution. Compound formation started immediately on addition of the amine. It was allowed to stand overnight, filtered off the crystalline product obtained, recrystallised it from methanol and dried as described previously (Yield 4.10g; 77.8%).

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S. No	• Compound	Colour	Yield		ound	-	S	Iculated %	ľ
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	Bis-A	Amine Comple	ses						
1.	Co(benzoate) ₂ ^(Py) 2	Reddish Pink	45. 2	12.55	62.47	4.12	12,83	62.70	4.35
2.	Co(o-toluate) ₂ ^(Py) 2	=	64.2	12,01	64.30	4.37	12.07	64.01	4.51
а. В	Co(o-chlorobenzoate)2 ^(Py) 2	=	77.8	11.05	54.41	3.05	11.16	54.53	3 03
4.	Co(m-chlorobenzoate)2 ^(Py) 2	=	73.9	10.93	54.29	2.91	11.16	54.53	3•03
• 0	Co(o-nitroberzoate) ₂ (Py) ₂	z	82.0	10.48	52.11	2.61	10.73	52.43	2.93
•9	Co(m-nitrobenzoate) ₂ (Py) ₂	=	8 3 • 8	10.54	52.19	2.69	10.73	52.43	2.93
7.	$Co(m-methoxybenzoate)_2^{(Py)}_2$	Ŧ	82.8	11.19	59.74	4.13	11.34	60.08	4.23
8.	$co(benzoate)_2^{(3-MEP_Y)}_2$	Pink	71.2	11.86	63.82	5,05	12.11	64 • 06	4.92
•6	co(o-toluate) ₂ ^(3-MePy) ₂	Ređ	73.5	11.13	65.31	5.28	11.44	65.19	5.43
10.	Co(o-chlorobenzoate) ₂ (3-MePy) ₂	=	67.3	10.33	55,93	4.51	10.53	56.10	3° 95
.11	Co(o-nitrobenzoate) ₂ (3-MePy) ₂	=	74.2	10,36	54.21	3.57	10.45	54.02	3.80
12.	Co(m-nitrobenzoate) ₂ (3-MePy) ₂	Ŧ	69 • 5	10.42	53.77	4.07	10.45	54.02	3.80
13.	Co(benzoate) ₂ (4–MPY)	Pink	65 • 5	11.85	63, 82	4.99	12.11	64 • 06	4.92
14.	$Co(o-toluate)_2(4-MePy)_2$	Red	78.2	11.35	65.11	5.31	11.44	65.19	5.43
15.	$Co(o-chlorobenzoate)_2(4-MePy)_2$	2 Pink	67.3	10.28	55.91	3.62	10.53	56.10	3.95
16.	$Co(o-nitrobenzoate)_2^{(4-MEPy)}_2$	Pink	67.2	10.23	54.11	3-5 9	10.45	54.02	3.80
17.	Co(m-nitrobenzoate) $_2$ (4-MePy) $_2$	Red	73.7	10.27	53.91	3.71	10.45	54.02	3.80
		Mono-Amine	Complexes						
18.	Co(benzoate) ₂ (2-NePy)	Purple	67.2	14.70	60•73	4.20	14.97	6087	4.31
19.	$co(o-toluate)_2(2-MePy)$	Green	62.5	13•75	62.32	5.00	13.96	62.52	4.97
20.	Co(o-chlorobenzoate) ₂ (2-MBPy)	Purple	73.9	12.69	51.67	3.51	12.74	51.81	3.23
21.	Co(m-chlorobenzoate) ₂ (2-MBPy)	=	51.5	12.63	52.03	3 •29	12.74	51.8I	3.23
22.	Co(o-nitrobenzoate) ₂ (2-MaPy)	Ŧ	71.3	12.17	49.43	3.20	12.18	49.56	3.09
23.	Co(m-nitrobenzoate) ₂ (2 -M eFy)	Ξ	72.6	12.13	49.26	3.01	12.18	49.56	3.09

4.62 3°06

58,11

12.97

4.81

58.07

12.61

66.6

 $Co(m-methoxybenzoate)_2$ (2-Me Py)

23. 24. ł

Ξ = Bis(m-chlorobenzoato)bis(pyridine)Co(II). A similar procedure to bis(o-chlorobenzoato) bis(pyridine)Co(II) preparation was carried out except that refluxing period was increased from 30 to 40 hr because of the decreased strength of the meta acid (pK_a 3.83) as compared to o-chlorobenzoic acid (pK_a 2.94).

Bis(o-nitrobenzoato)bis(pyridine)Co(II). It was prepared by a procedure similar to that used for the preparation of bis(o-chlorobenzoato)bis(pyridine)Co(II) but the refluxing period was decreased to 14 hr on account of the increased strength of the acid (pK_a , 2.17).

Bis(m-nitrobenzoato)bis(pyridine)Co(II). The compound was obtained using the procedure described for the preceding complex except the period of heating under reflux was increased to 20 hr because of the decrease in strength of the acid (pKa 3.87).

Bis(m-methoxybenzoato)bis(pyridine)Co(II). To a solution of m-methoxybenzoic acid (3.04g; 0.02 mole) in ethanol (130 ml) cobalt carbonate (1.29g; 0.0025 mole) was added and the mixture was heated under reflux for 40 hr. The unreacted cobalt carbonate was filtered off. On addition of two equivalents of pyridine (1.58g; 0.02 mole) to the filtrate a red solution was obtained which on standing gave reddish pink crystals of Co(O₂CC₆H₄CH₃O-m)_{2.2}C₅H₅N, which were separated, washed with ethanol, recrystallised from acetone and dried as described previously (Yield 4.30g; 82.8%)

Adducts of Co(II) complexes of benzoic, o-toluic, o-and mchloro and o-and m-nitro and m-methoxybenzoic acids were prepared with 2-, 3- and 4-MePy by the same procedure as described for the preparation of pyridine complexes of the corresponding Co(II) aryl carboxylates except the complexes of 2-MePy where equimolar quantities of the ligand were used.

The complexes prepared and their analytical data are presented in Table 1.

RESULTS AND DISCUSSION

Analytical results (Table 1) show that pyridine ligands with Co(II) aryl carboxylates give rise to two types of complexes: 1:2 bis-amine complexes of formula $Co(O_2CC_6H_4R)_2$ (L)₂ and 1:1 mono-amine complexes of composition $Co(O_2CC_6H_4R)_2$ L. Bis-amine complexes are formed by Py, 3-and 4-MePy while mono-amine complexes are given by sterically hindered ligand 2-MePy. The molar conductance values (Table 2) suggest that the complexes are covalent[11].

Bis-amine complexes. These complexes are pink to reddish pink or red in colour. All these complexes are soluble in common organic solvents and are quite stable towards air and moisture. Molecular weights of bisamine complexes (Table 2) show them monomeric in solution. The magnetic moments at room temperature fall in 4.86-5.07 B.M. range (Table 2) indicating that these complexes are octahedral.

Their electronic spectra (Table 3) show one main band centred around 20,000-21,000 cm⁻¹ and an additional band around 8060 cm⁻¹ for complexes whose spectra are also run in the near infrared region of 12,500-5,000 cm⁻¹. This main absorption band in pyridine complexes appears as a doublet but in 3-and 4-MePy complexes it has a shoulder on its high energy side. The main band is assigned to a ${}^{4}T_{1g} \longrightarrow {}^{4}T_{1g}(P)$ transition in an octahedral field and the band occurring at 8500 cm^{-1} is assigned to a ${}^{4}T_{1g} \longrightarrow {}^{4}T_{2g}$ transition. The splittings in the main visible band may be due to spin forbidden transitions enhanced by coupling to spin allowed transitions or spin orbit coupling. Hence, the higher end of the doublet or the shoulder on the principal band in adducts is assigned to spin forbidden quartet-doublet transition ${}^{4}T_{1g} \longrightarrow {}^{2}T_{1g}$ (H). The molar extinction coefficient values of the principal bands in these complexes fall in 27-45 1.mole⁻¹ cm⁻¹ range similar to the values observed in trans octahedral bispyridine complexes of Co(II) haloacetates [7]. This suggests that the 1:2 complexes have a *trans* octahedral comfiguration analogous to bispyridine Co(II) haloacetate complexes [7]. Other bis-amine complexes for which electronic spectra could not be recorded have also been considered to be of *trans* octahedral configuration by analogy.

In their IR spectra almost all of the bands originating from the coordinated ligands show positive shifts. For instance, the ring breathing modes observed at 995,1015 and 990 cm⁻¹ in free pyridine, 3- and 4-methylpyridines show a positive shift of 15-35 cm⁻¹ in their complexes indicating that the pyridine ligands coordinate through their nitrogen atoms[12–15]. Asymmetric and symmetric COO stretching frequencies fall in 1635–1600 and 1410–1390 cm⁻¹ ranges respectively.

In their far-IR spectra all these complexes show a number of bands originating from the ligands and the carboxylate groups making their unambiguous assignments extremely difficult. However, comparison of the spectra of the complexes with those of the ligand and the parent Co(II) aryl carboxylate shows that two new strong bands in 400-300 cm⁻¹ region and one or two equally intense bands in 300-200 cm⁻¹ region centred around 250 cm⁻¹ appear in all of them. These frequencies may be tentatively assigned to Co–O and Co–N vibrations respectively in agreement with the observations made by previous workers [16–19].

Mono-amine complexes of 2-MePy. All these complexes are purple except bis(o-toluato)(2-MePy)Co(II) which is of green colour. Like bis-amine complexes these are also soluble in common organic solvents but are comparatively less stable and undergo slow decomposition in air.

The magnetic moment of the green complex bis(otoluato)(2-MePv)Co(II) is 4.02 B. M. which is very close to the magnetic moment value of 4.11 B.M. of dimeric quinoline Co(II) benzoate complex[1]. This suggests that the green complex is a dimeric syn-syn carboxylate bridged species similar to the 1:1 complex of quinoline with Co(II) benzoate [1, 2, 20]. The magnetic moments of purple complexes lie in a very close range of 4.86-5.07 B.M. while the magnetic moment reported for the purple complex of 2-MePy with Co(II) benzoate^[2] is 5.03 B.M. Further, these values lie well within the widely varying range of 4.45-5.50 B. M. reported for 5-coordinated Co(II) complexes [21-23]. The exact magnitude of the magnetic moment depends on the extent of deviation from regular 5-coordinated symmetry [24]. These observations suggest that purple complexes of 2-MePy are monomeric 5coordinated trigonal bipyramidal molecules similar to the structure of the purple complex of 2-MePy with Co(II) benzoate reported by Thornton et al. [2, 20].

Electronic spectra of these complexes in methanol show a broad band near 19,680 cm⁻¹ and where the spectra were also recorded in low frequency region a band near 8500 cm⁻¹ is also observed in consonance with an octahedral environment of the ligating atoms around Co(II). However, the diffuse reflectance spectrum of the 2-MePy complex of Co(II) benzoate shows three bands at 9090, 11,500 and a broad band at 18,860 cm⁻¹ having a shoulder at 17,850 cm⁻¹ showing that the structure of the complex in solution and in solid phase is different. These bands are assigned to ${}^{4}A'_{2} \rightarrow {}^{4}E' {}^{4}A_{2} \rightarrow {}^{4}E' {}$

Compound*	Molar Conductance	Molecula	r Weight	<i>µ</i> _{eff}	Temp. K ⁰
	mole ⁻¹ ohm ⁻¹ cm ²	Found	Calcd.	(B•M•)	
1.	<u>B</u> 25•18	1s-Amine C 436.7	omplexes 458.9	5.00	293
2.	25.93	471.2	487.4	4.95	2 2 93
3.	28.13	5 09.7	528.2	4.90	294
4.	28 .76	523.2	528.2	4.92	293
5.	26.29	514.8	549.3	4.89	2 93
6.	27.18	538.5	549 .3	4.88	295
7.	28.02	506.2	519.4	4.91	293
8.	38.33	472.7	487.2	4.88	293
9.	28.96	523 .7	515.4	4.95	293
10.	34 • 20	-	-	4.94	293
11.	26.29	593.0	577.4	4.87	294
12.	28.02	-	-	4.92	293
13.	27.15	498.7	487.2	4.87	2594
14.	29.57	-	-	4.88	293
15.	31.11	543.2	556.3	4.87	295
16.	24.19	-	-	4.91	293
17.	25.94	563.4	57 7 . 4	4.90	294
	M	ono-Amine	Complexes		
18.	32.53	-	-	5.06	294
19.	27.31	-	-	4.02	295
20.	28.57	-	-	4.86	293
21.	29.34	-	-	4.89	296
22.	29.22	-	-	4.94	293
23.	31.15	-	-	4,86	294
24.	26.12	-	-	5.07	296

Table 2. Conductance, molecular weight and magnetic moments of adducts of Co(II) aryl carboxylates with pyridines

*Number refers to compounds in Table 1

7200 cm⁻¹, assigned to a ${}^{4}A_{2} \rightarrow {}^{4}A_{1}$ transition, was not observed in our complex because we could not get spectrum run below 8000 cm⁻¹. Excepting this the spectra of the two compounds are more or less identical with minor discrepancies in their band positions. This indicates that the two complexes have similar structures. Since lowering of D_{3h} to C_{3v} or C_{2v} symmetry causes some adjustments of the energy levels[25], the shoulder on the strong unsymmetrical band in our complex may be assigned to a ${}^{4}A_{2}(P)$ transition originating from ${}^{4}A_{2}(F)$ ground term in a weak field of D_{3h} symmetry.

The diffuse reflectance spectrum of the green complex bis(o-toluato) (2-MePy) Co(II) showed four bands at 8330, 13,333, 17,000 and 2222 cm⁻¹ in agreement with the four bands reported for the green complex of quinoline with Co(II) benzoate[2] and are likewise assigned to transitions ${}^{4}A_{2}(F) \longrightarrow {}^{4}E_{1}$, ${}^{4}A_{2} \longrightarrow {}^{4}B_{1}$, ${}^{4}A_{2} \longrightarrow {}^{4}E(P)$ and ${}^{4}A_{2} \longrightarrow {}^{4}A_{2}(P)$ originating from a square pyramidal geometry around Co(II). This leads to the conclusion that the green complex of 2-MePy with Co(II) o-toluate is dimeric and has a syn-syn carboxylate bridged structure similar to the 1:1 complex of quinoline with Co(II) benzoate[20].

IR spectra of the 2-MePy complexes is similar to the complexes of pyridine and other ligands in the normal as well as in the far-IR region pointing coordination of the 2-MePy ligand through its nitrogen atom. The Co-O and Co-N stretching frequencies likewise occur in the range of 400-300 and 300-200 cm⁻¹ respectively. Further, the difference between the asymmetric and symmetric COO stretching frequencies in these complexes varies between 200 and 225 cm⁻¹ which is similar to the values observed in mononuclear pyridine, 3- and 4-MePy Co(II) aryl carboxylate complexes, which being monomeric, cannot involve any other type of carboxylate bonding except bidentate chelating. This suggests that the carboxylate chelating. Whether the 2-MePy ligand in these complexes

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Compound *	Electronic	Spectra
	Medium	Bands Observed ★★ (cm ⁻¹)
	Bis-Amine Complexe	25
1.	Methanol	20,000(31), 21,050 sh
2.	4	20,840(45), 21,020 sh
3.	n	20,200(35), 21,030 sh
4.	n	20,200(41.5), 21,030 sh
5.	n	20,000(35), 21,030 sh
6.	н	20,000(27), 21,020 sh
7.	้๚	20,000(38), 20,800 sh
8.	Benzene	8,060 17,000, 17,860
9.	Methanol	20,200(31), 21,020 sh
10.	ч	20,200(27), 21,050 sh
11.	и	20,840(27), 22,790 sh
12.	u	20,000(25), 2 3 ,000 sh
13.	Benzene	8,060 17,010, 17,880
18.	Methanol	18,520(32), 21,500 sh
	Mono-Amine Complex	es
18.	Methanol Reflectance	8,540(4), 19,680(38) 9,090, 11,500, 17,950 sh, 18,860
19.	Methanol	8,690(5), 19,640(41)
20.	н	8,470(7), 19, 6 80(30)
21.	u	20,840(33), 22,000 sh
22.	H	20,000(19), 21,030 sh
23.	n	8,333(7), 19,680(43)
24.	i i	20,620(27), 21,600 sh

Table 3	Electronic	spectral	data of	adducts of	of Co(II) a	aryl carbox	ylates with	n pyridines
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*Number refers to compounds in Table 1.

*Molar extinction co-efficients (£1.mole⁻¹cm⁻¹) are given in parenthesis.

occupies an axial or an equatorial position of the D_{3h} structure cannot be established in absence of an X-ray structure analysis.

Comound +

Acknowledgements—The authors are thankful to Prof. O. P. Vig, Head, Department of Chemistry, Panjab University, Chandigarh (India) for providing facilities for carrying out various physical studies in his laboratories and Prof. A. B. P. Lever, Department of Chemistry, York University, Canada for helpful suggestions. One of us (A. K. G.) is grateful to Jammu University, Jammu for the award of a research scholarship for 2.5 years.

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