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NEW MIXED TETRADENTATE CHELATES OF Co(III) WITH ETHYLENDIIMINO- BIS – DIBENZOYLMETHANE

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ABSTRACT

Five new chelates of Co(III) of the $[Co(dibenzec)(amine)_2]^+$ *type (dibenzec.*H_2 *– ethylenediimino-bis- dibenzoylmethane:* $C_{32}H_{28}N_2O_2$*, amine=aniline, o-anisidine, p-toluidine, m- xilidine, α- naphtilamine) were synthetized and characterized by isolation of thirty-four new complex salts by means of the double decomposition reactions. The thermal stability of the complexes was studied by means of differential thermal analysis. The structural properties were discussed on the basis of IR and UV spectra.*

KEYWORDS : Co(III), chelates, complex salts, structure chromium (III)

RESUMO

Cinco quelatos novos de Co(III) do tipo $[Co(dibenzec)(amina)_2]^+$ *foram sintetzados e caracterizados através da isolação de trinta e quatro sais complexos usando reações de decomposição dupla. (dibenzec.*H_2*-etilenodiimino-bis-dibenzoilmetano :* $C_{32}H_{28}N_2O_2$*, amina=anilina, o-anisidina, p-toluidina, m-xilidina, α-naftilamina). A estabilidade térmica dos complexos foi estudada com análise térmica diferencial. As propriedades estruturais foram discutidas em termos de espectros na região infravermelha e ultravioleta.*

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INTRODUCTION

The β- diketones (e.g. acetylacetone, benzoylacetone, dibenzoylmethane) react easily with 1,2- and 1,3- aliphatic diamines and aromatic ortho – diamines. The formed bis – Schiff's bases act as tetradentate chelating agents towards bi and trivalent transition metal ions. Various complex salts and non-electrolytes of this class were obtained and characterized. Some derivatives were also used for analytical purposes [1-4].

The synthesis of ethylendiimino – bis – acetylacetone (ec.H_2) and some non – electrolytic complexes: Ni (ec.), Cu (ec), Pd (ec) was reported by Combers [5]. Mixed chelates of Co(lll) with ammonia $[Co(ec)(NH_3)_2]X$ were obtained by Morgan and Smith [6]. In our previous papers [7-9] a series of new mixed complexes of the type: $[Co(ec)(amine)_2]^+$ (aromatic and heterocyclic amines) were described.

Zsakó, Várhelyi and co-workers described in a previous paper new chelates of the ethylenediimino – bis – benzoylacetone (benzec.H_2: $C_{22}H_{24}N_2O_2$) [10].

In the present paper instead dibenzoylmethane was used for condensation with ethylendiamine. The bis Schiff's base formed: ethylendiimino – bis – dibenzoylmethane (dibenzec.H_2: $C_{32}H_{28}N_2O_2$) provides a series of new chelate cations with Co(lll) in the presence of organic N-bases.

EXPERIMENTAL PROCEDDURE

Ethylendiimine – bis- dibenzoylmethane (dibenzec.H_2): A sample of 0.2 mole of dibenzoylmethane and 0.1 mole of ethylenediamine in 250 mL methanol were refluxed on a water bath. After 2-3 hours boiling the Schiff base that separated was filtered off and washed with dilute methanol. Silky, irregular needles were obtained.

[Co(dibenzec)] ($C_{32}H_{28}N_2O_2$) : Dark yellow microcrystals were obtained by refluxing 0.1 mole cobalt acetate and 0.1 mole dibenzec.H_2 in 250 mL methanol for 30-40 minutes (Co calcd. 11.13%, found 11.08%).

[Co(dibenzec)(amine)$_2$]- acetate – solutions :

Method l.

Fifty mmoles of cobalt acetate and 50 mmole of dibenzec.H_2 in 400 mL ethanol were refluxed on a water bath for 30-40 minutes, subsequently 120-130 mmoles of different aromatic amines, pyridine or alkyl-pyridine derivatives were added. The mixture was oxidized by adding dropwise an excess of 30% (aprox. 10-12 mL) H_2O_2. The scarlet yellow microcrystals [Co(dibenzec)] formed dissolved slowly and a dark brown (from dark yellow a reddish brown depending on the nature of amine component). $[Co(dibenzec)(amine)_2]$- acetate – solution was formed. After cooling the solutions were filtered and used for double decomposition reactions.

Method ll.

The suspension of 50 mmoles of [Co(dibenzec)] and 5g of sodium acetate in 400 mL ethanol was treated with 120-130 mmole of amine and oxidezed with 10-12 mL of 30% H_2O_2 added dropwise under refluxing conditions and the cooled. The filtered solutions were used for double decompositions reactions.

[Co(dibenzec)(amine)$_2$]X complex salts: A sample of 10 mmoles of $[Co(dibenzec)(amine)_2]$ acetate in 100 mL alcoholic solutions was treated with an excess of 2-10% aqueous KI, $NaClO_4$, $NH_4[Co(NH_3)_2(NO_2)_4]$, $[Cr(NCS)_4(amine)_2]NH_4$

in 3% aqueous-alcoholic solutions. The obtained crystalline products were filtered off after 15-30 minutes, washed with dilute ethanol and dried in air.

Analytical Determinations

The cobalt content of the samples was determined complexometrically after decomposing 80-100 mg of the substance with boiling conc. sulphuric acid and some crystals of KNO_3.

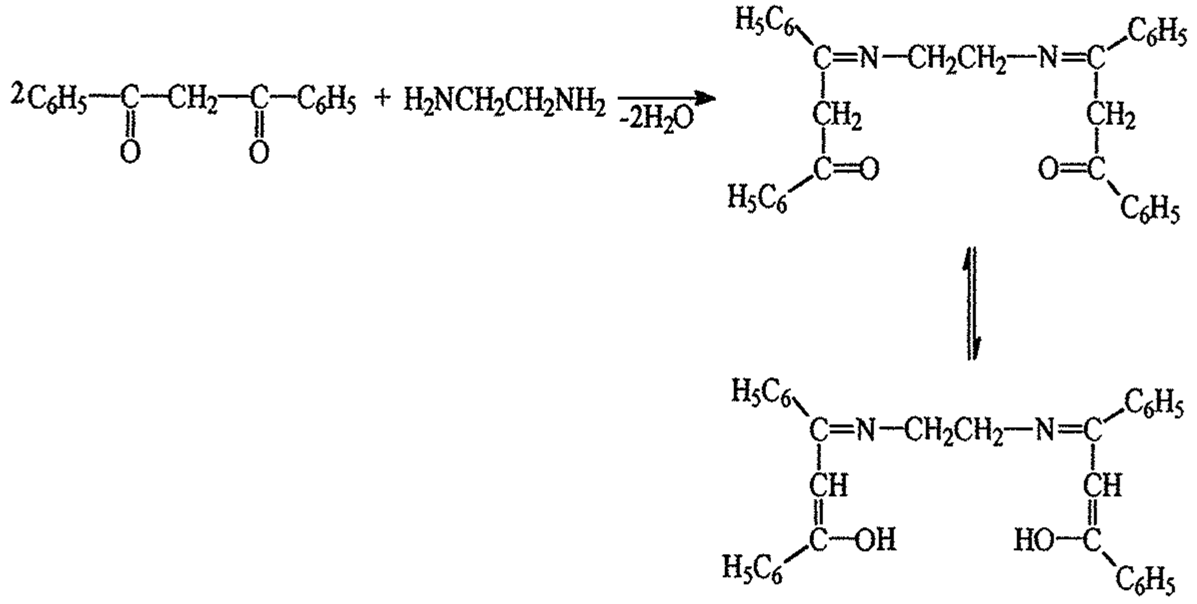
After dilution with water the solution was neutralized with sodium acetate. The N contents were determined by usual microanalytical methods.

The electronic spectra were recorded in methanol with a Specord recording spectrophotometer (Carl Zeiss Jena).

The infrared spectra were registered in KBr tablet on a IR Perkin-Elmer 1600 apparatus.

RESULTS AND DISCUSSIONS

The condensation reaction take place according to the following equation:

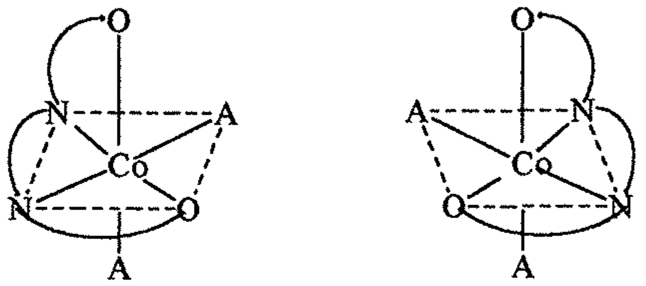


The enolic form of this bis Schiff's base exhibits chelating properties towards transitions metal ions. Of the analogous derivatives of the higher homologues of the diamines only 1,2- and 1,3-propanediamine are suitable for chelation. The condensation products with 1,4-, 1,5-, 1,6- diamines do not present complexing properties.

Some bivalent transition metals form well defined, non-electrolytic type chelates with the above mentioned reagent, e.g. Cu(dibenzec), Co(dibenzec), Pd(dibenzec), Pt(dibenzec). From these M(dibenzec) type compounds the Co(II) derivative can be oxidized easily to mixed electrolytic chelates of cobalt (II), in the presence of monodentate ligands. For this purpose perhydrol, chlorine and bromine can be used in the presence of amines, phosphines, arsines, e.g.:

$$2Co^{2+} + 2\text{dibenzec}H_2 + 4\text{amine} + H_2O_2 \rightarrow 2[Co(\text{dibenzec})(\text{amine})_2]^+ + 2H^+ + 2H_2O$$

In this paper five new chelate cations [Co(dibenzec)(amine)$_2$]$^+$ (amine=aniline, o-anisidine, p- toluidine, m- xilidine, α- naphthylamine, pyridine, γ- picoline) were prepared. These new chelate cations were characterized by isolation of 34 salts by means of double decomposition reaction from the alcoholic solutions of the acetates with alkaline salts of the halides, pseudohalides and complex acids of Co(lll) and Cr(lll), respectively. The [Co(dibenzec)(amine)$_2$]$^+$ type chelate cations exhibit five stereoisomeric modifications, viz. two optical antipode pairs and an inactive, symmetrical "*trans*" form (Fig.1).



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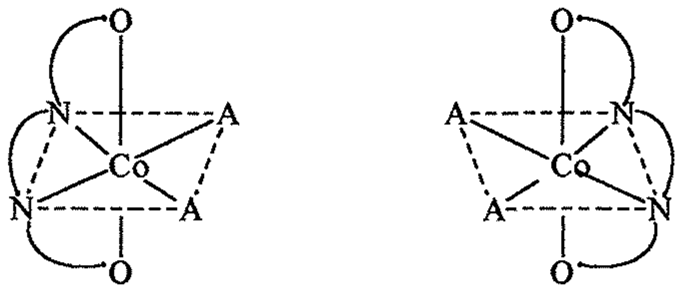

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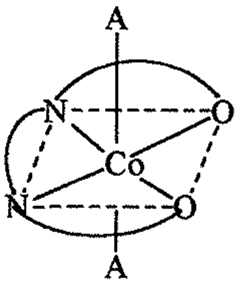

Inactive

Figure 1. The stereoisomers of the [Co(dibenzec)(amine)$_2$]$^+$ type chelate cations.

The new complex salts obtained are characterised in Table 1.

Table 1. New complex salts of the type [Co(dibenzec)(amine)$_2$]X.

No	Formula	Molecular Weight calc.	Yield (%)	Aspect	Analysis (%)	
					calc.	found
I	II	III	IV	V	VI	VII
1	[Co(dibenzec)(pyridine)$_2$]I	814.48	72	sparkling, red-brown prisms	Co 7.23 N 6.87	7.19 6.73
2	[Co(dibenzec)(pyridine)$_2$]ClO$_4$	787.03	76	sparkling, dark brown spears	Co 7.48 N 7.11	7.30 4.06
3	[Co(dibenzec)(pyridine)$_2$]NCS	745.66	40	brown square plates	Co 7.90 N 9.38	7.77 9.21
4	[Co(dibenzec)(pyridine)$_2$] [Co(NO$_2$)$_4$(NH$_3$)$_2$]	964.61	75	brown needles	Co 12.22 N 14.51	12.10 14.43
5	[Co(dibenzec)(pyridine)$_2$] [Cr(NCS)$_4$(NH$_3$)$_2$]	1006,01	86	reddish brown microcrystals	Co+Cr 11.02 N 13.91	10.93 13.83
6	[Co(dibenzec)(pyridine)$_2$] [Co(NCS)$_4$(aniline)$_2$]	1158.01	90	Brown needles	Co+Cr 9.58 N 12.09	9.47 11.94
7	[Co(dibenzec)(γ-picoline)$_2$]I	842.50	52	Brown irregular crystals	Co 6.99 N 6.64	6.92 6.58
8	[Co(dibenzec)(γ-picoline)$_2$]ClO$_4$	815.05	60	orange-brown short prisms	Co 7.23 N 6.87	7.15 6.71
9	[Co(dibenzec)(γ-picoline)$_2$]NCS	773.68	38	thick, dark brown disks	Co 7.61 N 6.46	7.55 6.34
10	[Co(dibenzec)(γ-picoline)$_2$] [Co(NO$_2$)$_4$(NH$_3$)$_2$]	992.63	82	short, brown irreg. prisms	Co 11.87 N 14.10	11.78 14.00
11	[Co(dibenzec)(γ-picoline)$_2$] [Cr(NCS)$_4$(aniline)$_2$]	1185.03	88	reddish brown microcrystals	Co+Cr 9.36 N 11.81	9.22 11.74
12	[Co(dibenzec)(o-anisidine)$_2$]I	902.66	53	dark brown square prisms	Co 6.52 N 6.20	6.44 6.12
13	[Co(dibenzec)(o-anisidine)$_2$]ClO$_4$	875.21	58	square thin brown plates	Co 6.73 N 6.39	6.65 6.20
14	[Co(dibenzec)(o-anisidine)$_2$]SCN	817.77	47	thick, dark brown disks	Co 7.20 N 8.55	7.17 8.43
15	[Co(dibenzec)(o-anisidine)$_2$] [Cr(NCS)$_4$(NH$_3$)$_2$]	1094.19	94	brown irreg. cryst.	Co+Cr 10.14 N 12.79	10.06 12.69
16	[Co(dibenzec)(o-anisidine)$_2$]I	870.54	73	sparkling brown prisms	Co 6.77 N 6.43	6.71 6.33
17	[Co(dibenzec)(p-toluidine)$_2$]ClO$_4$	843.09	82	brown disks plates	Co 6.99 N 6.64	6.85 6.57
18	[Co(dibenzec)(p-toluidine)$_2$]SCN	801.72	50	brown square	Co 7.35 N 8.73	7.19 8.62
19	[Co(dibenzec)(p-toluidine)$_2$] [Co(NO$_2$)$_4$(NH$_3$)$_2$]	1020.67	84	light brown microcrystals	Co 11.54 N 13.71	11.43 13.60
20	[Co(dibenzec)(p-toluidine)$_2$] [Cr(NCS)$_4$(NH$_3$)$_2$]	1062.07	94	reddish – brown micro-crystals	Co+Cr 10.44 N 13.18	10.31 13.10
21	[Co(dibenzec)(p-toluidine)$_2$] [Cr(NCS)$_4$(aniline)$_2$]	1214.07	87	reddish – brown micro-crystals	Co+Cr 9.13 N 11.53	9.06 11.40
22	[Co(dibenzec)(α-naphtylamine)$_2$]I	942.54	83	brown disk	Co 6.25 N 5.94	6.18 5.82

I	II	III	IV	V	VI	VII
23	[Co(dibenzec)(α-naphtylamine)$_2$]ClO$_4$	915.09	86	red-brown microcrystals	Co 6.25 N 5.94	6.18 5.82
24	[Co(dibenzec)(α-naphtylamine)$_2$]NCS	873.72	73	reddish-brown microcrystals	Co 6.74 N 8.01	6.71 7.95
25	[Co(dibenzec)(α-naphtylamine)$_2$] [Cr(NCS)$_4$(NH$_3$)$_2$]	1134.07	94	red-brown microcrystals	Co+Cr 9.78 N 12.34	9.66 12.21
26	[Co(dibenzec)(α-naphtylamine)$_2$] [Cr(NCS)$_4$(aniline)$_2$]	1286.07	96	red-brown microcrystals	Co+Cr 8.62 N 10.88	8.55 10.79
27	[Co(dibenzec)(m-bromoaniline)$_2$]I	972.40	74	dark brown irreg. prisms	Co 6.06 N 5.75	6.00 5.63
28	[Co(dibenzec)(m-bromoaniline)$_2$]ClO$_4$	944.95	80	sparkling, short brown prisms	Co 6.23 N 6.87	6.20 6.77
29	[Co(dibenzec)(aniline)$_2$]I	842.50	51	sparkling, thin brown prisms	Co 6.99 N 6.64	7.02 6.51
30	[Co(dibenzec)(aniline)$_2$]ClO$_4$	815.05	62	sparkling, brown rhomb. plates	Co 7.23 N 6.87	7.26 6.79
31	[Co(dibenzec)(aniline)$_2$] [Cr(NCS)$_4$(aniline)$_2$]	1186.03	84	brown dendrites	Co+Cr 9.35 N 11.80	9.20 11.69
32	[Co(dibenzec)(m-xylidine)$_2$]I	898.74	53	dark brown plates	Co 6.55 N 6.23	6.44 6.19
33	[Co(dibenzec)(m-xylidine)$_2$]ClO$_4$	871.29	62	sparkling brown plates	Co 6.76 N 6.42	6.70 6.33
34	[Co(dibenzec)(m-xylidine)$_2$] [Cr(NO$_2$)$_4$(aniline)$_2$]	1242.27	92	reddish-brown microcrystals	Co+Cr 8.89 N 11.26	8.77 11.11

When compared to the analogous ethylendiimino – bis- acetylacetone derivatives, [Co(ec)(amine)$_2$]X, the [Co(dibenzec)(amine)$_2$]X salts are more sparingly soluble in water and dilute alcohol.

The salts with [Co(NCS)$_4$(amine)]$^-$ are insoluble in water and alcohol, and easily soluble in ketones, e.g. acetone, acetylacetone, dimethylformamide and dimethylsulfoxide, respectively.

Thermal Stability

The thermal stability of some [Co(dibenzec)(amine)$_2$]X type complexes was studied by means of differential thermal analysis. The complicated thermal degradation processes begins at 140-180°C in the case of the [Co(dibenzec)(amine)$_2$]X derivatives as a function of the nature of the amine component and of the external anion. The nitrates, perchlorates, periodates (not analysed) decompose suddenly, generally with explosion. The halides, pseudohalides and the corresponding salts with complex acids liberate free amines, N$_2$, CO, CO$_2$ and other decomposition and oxidation products in non stoichiometric ratios, during a slower pyrolysis process under the static air atmosphere of the furnace. The final product at 800-850°C is Co$_3$O$_4$ or Co$_3$O$_4$ + Cr$_2$O$_3$.

The thermal behaviour of the [Co(dibenzec)(amine)$_2$]X type complexes is analogous with that of the [Co(ec)(amine)$_2$]X derivatives, the latter having a higher thermal stability.

The exo- and endothermal peaks in the temperature range of 150-550°C show these complicated decomposition and oxidation processes.

The first not well formed inflection point on the thermograms of some derivatives with X=Br, I, NCS corresponds to a partial deamination reaction.

$[Co(dibenzec)(amine)_2]X \rightarrow [Co(dibenzec)(amine)X] + amine$

This endothermal process (DTA- peak at 150-180°C is not so evident as in the case of the dimethylglioximino complexes $[Co(DH)(amine)_2]X$ which were reported in our earlier papers [11-12], also from the kinetic point of view:

$[Co(DH)_2(amine)_2]X \rightarrow [Co(DH)_2(amine)X] + amine$

Electronic Spectra

The spectrum of dibenzec.H_2 has a similar feature to that of benzec.H_2 and ec.H_2 respectively, but its characteristic double bond, situated at about 30800 and 32700 cm^{-1} in case of the latter, is strongly shifted towards the visible region and appears at 28400 cm^{-1} and 29400 cm^{-1} for the former. This important shift is due to the effect of the phenyl group, extending the π-bond system of the molecule. Presumably, the above mentioned bands correspond to a π-π^* transition.

Table 2. IR spectral data of some $[Co(dibenzec)(amine)_2]X$ type complexes and free dibenzec.H_2.

Substance vibration	I	II	III	IV	V	VI
νN-H	-	3220- 3180m 3125m	3220- 3160m 3130m	3200- 3160m 3120m	3200m 3130 3080	3260m 3170m 3085m
νC-H	2960m 2880m	2960w 2860w	2970m 2880w	2960m 2870w	2980m 2860m	2985w 2880w
νC_{Ar}-C_{Ar}	1620vs	1605vs	1605vs	1605vs	1610vs	16020vs
$\delta_{as}NH_2$	-	1580m	1585m	1580m	1590w	1540vs
νC-N	1555vs	1530vs	1535vs	1535vs	1540vs	1540vs
$\delta_{as}CH_3$	1451s	1495vs 1470s	1470s	1470s	1475m 1450s	1485s 1435s
$\delta_s CH_2$	1355vs	1350m	1360m	1360m	1370m	1365m
δNH_2	-	1310s	1310s	1310s	1318s	1310vs
νC-O	1180w 1160w	1130s	1134s	1145s	1145w 1135w	1340m
γNH_2	-	845m	850m	850m	825m	865m
γC_{Ar}-C_{Ar}	770vs	770vs	765vs	765vs	760vs	760m
γC_{Ar}-H	715vs	720s	720s	720s	715s	720vs

I. Dibenzec.H_2; II $[Co(dibenzec)(aniline)_2]I$; III $[Co(dibenzec(m\text{-}toluidine)_2]I$; IV $[Co(dibenzec)(o\text{-}Br\text{-}aniline)_2]I$; V $[Co(dibenzec)(m\text{-}xylidine)_2]I$; VI $[Co(dibenzec)(\alpha\text{-}naphtylamine_2]I$

The coordination of both ec.H_2 and dibenzec.H_2 gives rise to the formation of larger delocalized π-bond systems, involving also the π type d_{xy} and d_{yz} orbitals of the Co atom. In this case the π-π* absorption bands may be expected to be shifted toward lower wave number values. In the case of the analogous ec and pec (pec.H_2=1,3-propylenediimino-bis-acetylacetone) complexes of Co(III) two absorption bands appear indeed at about 2300 and 2960 cm^{-1}, respectively.

Freshly prepared solutions of the [Co(II)dibenzec] complex exhibit several d-d transition bands, viz. at 13600, 1490 and 16500cm^{-1}. In the UV region two main bands appear, at 24100 and 30200 cm^{-1}, respectively, as well as three inflection points at 21000, 23000 and 28000 cm^{-1}. Upon contact with air, the spectrum changes gradually in 48 hours, the d-d bands disappear and there remains a single strong band at 2800 cm^{-1} and two inflection points at 17000 and 29000 cm^{-1}. Presumably, this transformation is due to the oxidation of Co(II) to Co(III) and the strong band may correspond to the π-π* transition in the conjugated π-bond system of the resulting $[Co(dibenzec)(H_2O)_2]^+$ complex ion. Generally, in the visible and UV region, the amine containing dibenzec complex of Co(III), ($[Co(dibenzec)(amine)_2]^+$), exhibits five absorption bands, as the corresponding ec and pec derivatives. Sometimes, besides them inflection points between 13800 and 15000 cm^{-1} also appear, indicating weak d-d transitions.

The absorption bands of the dibenzec complexes studied are summarized in Table III.

Table III. Wave numbers(in cm^{-1}) and molar absorptivity (ε) of the absorption bands in the electronic spectrum of $[Co(dibenzec)(amine)_2]X$ type complexes.

No	Amine	X	Bands				
			A	B	C	D	E
1	NH_3*	I	21800 1700	27300 23000	34000 20000	43500 32000	49300 74000
2	aniline	I	22000	27000	35500	43000	49000
3	m-toluidine	I	21500	27300	34200	40600	48800
4	p-toluidine	ClO_4	22000	27400	35600	40300	49000
5	pyridine*	ClO_4	22700 1500	27400 11600	-	50000 39300	74000 46500
6	γ-picoline	ClO_4	22700	27400	-	39500	45300
7	α-naphtylamine	Ac	21500	29200	36100	41500	46600
8	m-xylidine	I	21200	27100	35400	28500	37600
9	o-anisidine	I	22000	27200	35200	38500	48500
10	m-bromoaniline	I	22000	27500	35500	44500	48500
11	p-bromoaniline	I	22200	27300	35000	37800	48000
12	β-picoline	Ac	22600	27400	-	39500	45300

Ac=CH_3COO^-; *Ref. 13.

Obviously, both bands A and B have lower wave numbers as compared to the absorption bands of dibenzec.H_2 exactly as with the analogous ec. complexes, suggesting that these might be due to π-π* transitions. As far as the influence of the amine ligands is concerned, in the case of ec and pec complexes of Co(III), a difference has been observed [7] between the behaviour of the amine ligands forming only σ-bands with Co and those forming also π-bonds. The former situation appears in the case of complexes 1-9 in Table III, the latter one with complexes 10-12.

The mean values of the wave numbers of the five absorption bands obtained for the dibenzec complexes studied, are presented in Table IV, separately for σ- bond forming amine derivatives (δ), and π-bond forming ones (π).

Table IV. Mean wave numbers (in cm^{-1}) of the absorption bands for dibenzec and ec. complexes of Co(III) containing only σ- bond forming amine ligands (δ), also π-bond forming ones (π) and general mean values(g).

Bond		A	B	C	D	E
dibenzec	σ	21720	27400	34900	41920	48500
	π	22000	27700	36100	39000	47000
	g	21850	27500	35300	40800	48000
ec	σ	23600	29700	35400	42000	45700
	π	22900	29600	35000	38900	45300
	g	23300	29700	35200	40500	45600

For the sake of comparison besides the general mean value (g) the analogous data reported earlier for ec. complexes are also given in the same Table.

By comparing the mean wave numbers one can see, that substitution of ec with dibenzec entails the shift of bands A and B towards lower values; bands C and D are practically not affected and band E exhibits an important shift towards higher wave numbers. Therefore we presume that bands A and B might be due to π-π* transitions as shown above, bands C and D besides the Co atom might be involved the amine ligands and with band E the ec and dibenzec ligands, respectively.

Concerning the influence of the σ or π type of the amine ligands, practically, the bands B and C are not affected at all. In the case of band D, and in a smaller extent also band E, the π type amine ligands give rise to a shift towards lower wave numbers, both with ec and dibenzec derivatives. The behaviour of band A is more complicated. It is also shifted towards lower wave number by π type amines in the case of ec-complexes, but the opposite is observed with dibenzec ones, these effects however are not important and might be due to experimental artifacts.

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