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ORGANOMETALLIC DERIVATIVES OF COBALT CHELATES OF BIS(ACETYLACETONE) ETHYLENDIAMINE

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In connection with research projects being conducted in this laboratory on the stabilization of cobalt–carbon bond by chelation, several chelating agents were tried. Among these the tetradentate bis(acetylacetone) ethylendiamine, $[CH_3COCH_2\text{-}C(CH_3){=}NCH_2]_2$ (BAE), was also considered and some preliminary results are reported in the present paper.

Co^{II}(BAE), $[Co^{III}(BAE)L_2]X$ AND Co^{III}(BAE)LX

Investigations on the preparative chemistry of cobalt chelates of BAE appear to be surprisingly scanty.

Co^{II}(BAE) and $[Co^{III}(BAE)(NH_3)_2]X$ (X = Cl, Br, I, NO_2, NO_3, ClO_3, ClO_4, *d*-camphosulphonate) were reported by Morgan and Smith[1] but McCarthy *et al.*[2] were unable to purify Co^{II}BAE satisfactorily owing to rapid decomposition in solution. Attempts to obtain Co^{II}BAE by chelate exchange were also unsuccessful[3]. On the other hand, various salts of $[Co^{III}(BAE)(NH_3)_2]^+$ were prepared also by Ripan *et al.*[4].

We prepared Co^{II}BAE, (I), and the following octahedral complexes: $[Co(BAE)(NH_3)_2]Cl$ (II), $[Co(BAE)(NH_3)_2]Br$ (III), $[Co(BAE)(Py)_2]Br$ (IV), $[Co(BAE)(BA)_2]Br$ (V), $[Co(BAE)(Ph_3P)Br]$ (VI) (Py = pyridine, Ph_3P = triphenylphosphine, BA = benzylamine) by reacting the Co^{II} halide with BAE and the appropriate base in methanol.

Analyses and m.p.s. are given in Table 1. The complexes are diamagnetic. UV and visible absorption frequencies and intensities are listed in Table 2 and Fig. 1.

The complexes are indefinitely stable, and insoluble in nonpolar solvents but soluble in methanol. The complexes (II) to (V) are soluble in water. It was observed that the NH_3 ligand can be easily displaced by pyridine from (II) and (III). Although the complexes (II) to (VI) should exist in five forms, two pairs of optical isomers and one inactive form, all the products are considered[1] to be in the most stable optically inactive *trans* structure, containing a planar tetradentate chelate.

RCo^{III}(BAE)L AND RCo^{III}(BAE)

By reaction with Grignard reagents "RMgBr" (R = CH_3, C_2H_5, C_6H_5) in tetrahydrofuran (THF) or with phenyllithium in ether, all the complexes $[Co^{III}(BAE)L_2]X$ or $[Co^{III}(BAE)LX]$ (II) to (VI) give red organocobalt derivatives which are soluble in dil. aqueous acids and can be precipitated with ammonia. When dried in air at

TABLE I

SOME $[Co^{III}(BAE)L_2]X$, $Co^{II}(BAE)L_2$ AND $RCo^{III}(BAE)$ COMPLEXES

No.	*Formula*	*C%*		*H%*		*N%*		*Co%*		*M.p.*	*Remarks*
		Found	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*		
(I)	CoBAE	51.44	51.25	6.33	6.05	10.13	9.05	20.46	20.96	151–2°	orange needles from benzene
(II)	$CoBAE(NH_3)_2Cl$	40.55	41.09	7.01	6.90	7.81[a]	7.98	16.39	16.42	205° dec.	deep yellow needles from water/ethanol
(III)	$CoBAE(NH_3)_2Br$	36.31	36.47	6.48	6.12	6.92[a]	7.09	14.71	14.91	213–4° dec.	yellow needles from water/ethanol
(IV)	$CoBAE(Py_2)Br$	50.87	50.88	5.57	5.43	10.08	10.79	11.21	11.35	184–6° dec.	brown crystals precipitated from water
(V)	$CoBAE(BA)_2Br$	54.35	54.13	6.48	6.55	10.15	10.12	10.44	10.65	192–3°	deep yellow plates from acetone/ligroine
(VI)	$CoBAE(PPh_3)Br$	57.05	57.80	5.83	5.33	4.41	4.49	9.21	9.45	135°	black crystals from ether/methanol
(X)	$CoBAECH_3$	52.81	52.72	7.93	7.15	9.44	9.46	19.70	19.89	194° dec.	green needles from benzene
(XI)	$CoBAEC_2H_5$	54.06	54.18	7.73	7.47	9.04	9.03	18.81	18.99	99–100°	green solid (not recrystallized)
(XII)	$CoBAEC_6H_5$	60.31	60.19	6.55	6.47	7.96	7.82	16.44	16.45	237°	green solid (not recrystallized
(XIII)	$CoBAEPyC_6H_5$	63.48	63.15	6.75	6.45	9.15	9.60	13.48	13.62	237°	orange crystals from pyridine

[a] Only the nitrogen of the NH_3 ligands was determined by displacement with NaOH.

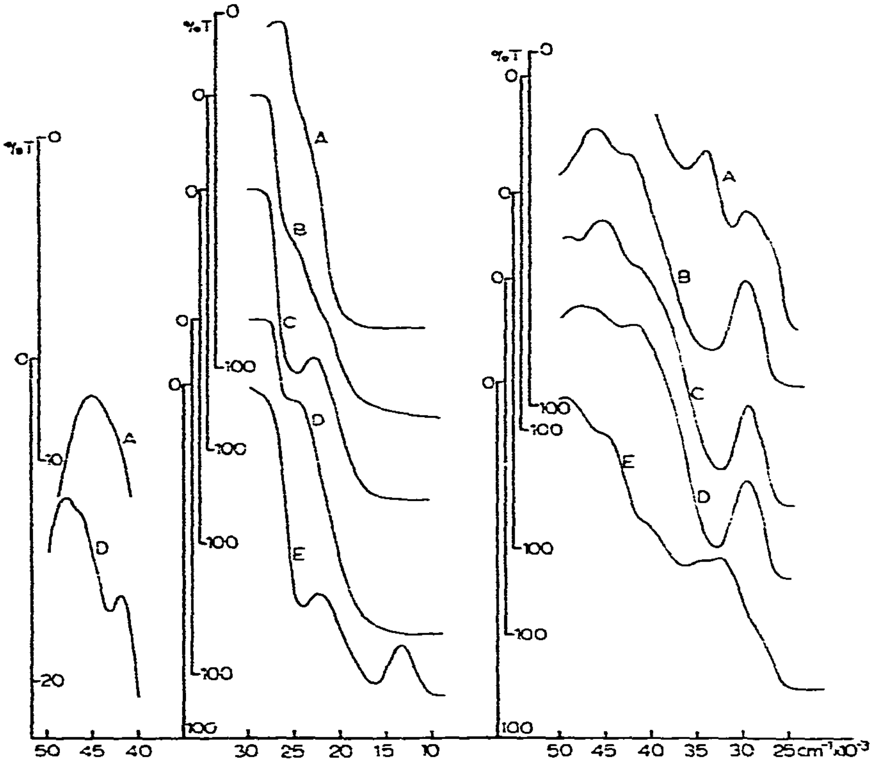

Fig. 1. UV and visible absorption spectra of A) I, B) II, C) IV, D, V, E) VI.

room temperature, red crystalline complexes of general formula RCo(BAE)H_2O are obtained, irrespective of the ligand(s) L present in the starting complex. By this method the compounds $CH_3Co(BAE)H_2O$ (VII), $C_2H_5Co(BAE)H_2O$ (VIII), $C_6H_5Co(BAE)H_2O$ (IX) were prepared, but they lost the water molecule by long standing in the desiccator (P_2O_5).

By heating (50–100°), all the complexes (VII) to (IX) show change in colour from red to green and the crystalline compounds become eventually green powders. These products are indefinitely stable in dry air. The analysis are in accord with the general formula RCo(BAE) (Table 3). By this procedure the complexes $CH_3Co(BAE)$ (X); $C_2H_5Co(BAE)$ (XI); $C_6H_5Co(BAE)$ (XII) were prepared (Table 1).

They show slow decomposition in the common non polar solvents in the presence of air. The complexes appear to be monomeric in benzene. The UV and visible absorption frequencies and intensities are reported in Table 2 and Fig. 2. Magnetic susceptibilities were as follows: $CH_3Co(BAE)$, χ $-0.15 \pm 0.03 \times 10^{-6}$; C_2H_5CoBAE, χ $-0.11 \pm 0.03 \times 10^{-6}$; C_6H_5CoBAE, χ $-0.33 \pm 0.04 \times 10^{-6}$.

When RCo(BAE) complexes are dissolved in aqueous acids red solutions are formed from which the corresponding RCo(BAE)H_2O complexes can be obtained by neutralization with ammonia. The addition of one more ligand to the RCo(BAE) was observed also by dissolving the complexes in benzene solutions containing pyridine, benzylamine or ethylenediamine, or directly in pyridine or benzylamine.

TABLE 2

ULTRAVIOLET AND VISIBLE ABSORPTION FREQUENCIES ($cm^{-1} \times 10^{-3}$) AND INTENSITIES (log ε_{max}, in bra

BAE	51 [3.89]				
CoBAE			45.8 [4.34]	(obs?)	
CoBAE$(NH_3)_2$Cl			45.9 [4.48]	42.3 (sh) [4.38]	
CoBAE$(NH_3)_2$Br			45.9 [4.48]	42.4 (sh) [4.38]	
CoBAE$(pyr)_2$Br		~ 49.4 [4.54]	45.4 [4.63]	41.4 (sh) [4.40]	
CoBAE$(BA)_2$Br		47.8 [4.63]	(obs?)	41.9 [4.52]	
CoBAE(PPh_3)Br		49.4 [4.73]	44.8 (sh) [4.60]	39.9 (sh) [4.14]	
C_6H_5Co(BAE)		~ 48.3 [4.54]	43.9 [4.53]		36.55 [4.1
C_2H_5CoBAE			45.8 [4.39]		36.6 [4.1
CH_3CoBAE			46.25 [4.42]		36.4 [4.0

$CH_3Co(BAE)$ was reduced with $NaBH_4$ and Co^{II}BAE was obtained in good yield. From this the $[Co(BAE)(NH_3)_2]Cl$ was again obtained with NH_4Cl and NH_3 in the presence of air.

DISCUSSION

The above results are further evidence of the possibility of stabilization of the cobalt–carbon bond by chelation with different ligands. The organometallic chelates reported in the present paper can be usefully studied in connection with the investigations of cobalamin-coenzyme model molecules[6,7]. Particularly interesting is the labilization of the donor ligand in the *trans* position to the alkyl or aryl group and the easy formation of a novel series of pentacoordinate Co^{III} complexes. The chemical behaviour of the above substances including ligand substitution and reactivity of the cobalt–carbon bond are being studied. The physical chemistry of the complexes including the interpretation of UV spectra, magnetochemistry and electrochemistry are also under investigation in this laboratory.

TABLE 3

SOME RCo(BAE)·H_2O COMPLEXES

No.	*Compound*	*N %*		*Co %*		*H_2O %*	
		Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
(VII)	$CH_3Co(BAE)\cdot H_2O$	8.91	8.82	18.75	18.63	5.73	5.85
(VIII)	$C_2H_5Co(BAE)\cdot H_2O$	8.53	8.38	17.95	17.71	5.48	5.61
(IX)	$C_6H_5Co(BAE)\cdot H_2O$	7.44	7.45	15.66	15.54	4.78	5.02

EXPERIMENTAL

Ligands

The BAE was prepared by a previously described procedure[8]; m.p. 113° (from toluene). Grignard reagent in anhydrous THF and C_6H_5Li in anhydrous ethyl ether

E COMPLEXES OF Co^{III}

	[4.45]	30.95 [4.49]			
	[4.01]	29.75 [3.70]	26.6 (sh) [3.57]	(~ 22 sh?)	16.5 (sh) [1.59]
		29.30 [3.88]	24.6 (sh) [2.83]	(~ 22 sh?)	(obs?)
		29.40 [3.88]	24.6 (sh) [2.82]	(~ 22 sh?)	(obs?)
		29.35 [3.85]	(obs?)	22.6 [2.74]	15.9 (sh) [1.53]
		29.20 [3.91]	(obs?)	24.6 [3.07]	16.3 (sh) [1.60]
	[4.00]	31.60 [4.00]	28.5 (sh) [3.77]	21.6 [2.88]	12.9 [2.50]
sh)	[3.85]	27.0 [3.57]	25.7 (sh) [3.56]		15.3 [2.92]
	[3.90]	28.6 (sh) [3.56]	25.2 (sh) [3.41]	22.3 (sh) [3.08]	14.8 [2.80]
sh)	[3.87]	29.2 (sh) [3.57]	25.5 (sh) [3.43]	22.8 (sh) [3.14]	14.9 [2.88]

were freshly prepared just before each reaction and titrated by conventional acidimetric methods. All the other reagents were obtained commercially and used without further purification.

Complexes

$Co^{II}BAE$ (I) was prepared following the procedure described by Morgan and Smith[1] and was crystallized from benzene, by concentration of the hot benzene solution under vacuum.

$Co^{III}BAE(NH_3)_2Cl$ (II) and $Co^{III}BAE(NH_3)_2Br$ (III) were prepared dissolving 5.12 g BAE (20 mmole) and 4.76 g $CoCl_2 \cdot 6H_2O$ (20 mmole) or respectively 6.61 g $CoBr_2 \cdot 6H_2O$ (20 mmole) in hot methanol, adding dropwise a concentrated aqueous

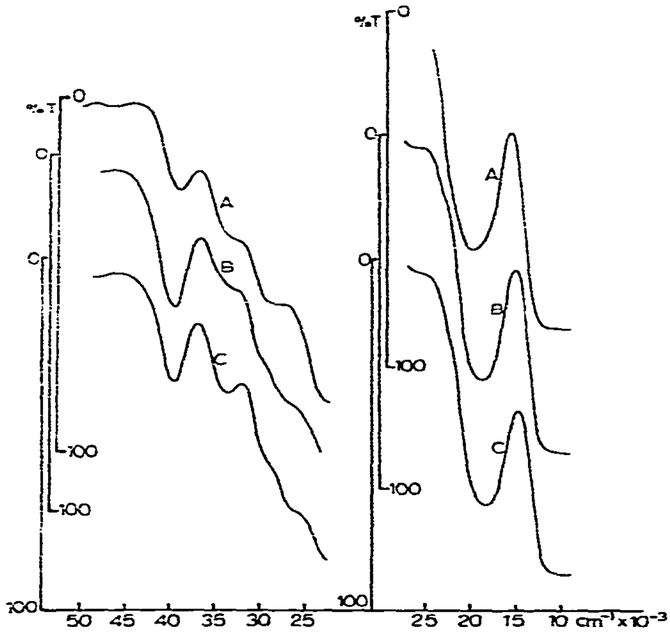

Fig. 2. UV and visible absorption spectra of A) XII, B) X, C) XI.

ammonia solution and heating for 2 h under stirring. After cooling, the solid product was filtered and crystallized from water/ethanol.

$Co^{III}BAE(Py)_2Br$ (IV). $CoBr_2 \cdot 6H_2O$ (3.3 g, 10 mmole) was dissolved in hot methanol together with 2.56 g BAE (10 mmole), 0.56 g KOH (10 mmole) and excess of pyridine (3 ml). After concentration of the solution a brown solid was obtained by addition of 3 ml H_2O.

$Co^{III}BAE(Ph_3P)Br$ (VI). A solution of 2.56 g (10 mmole) of BAE and 3.3 g (10 mmole) of $CoBr_2 \cdot 6H_2O$ in hot methanol was treated with a solution 2.61 g (10 mmole) of Ph_3P in ether (50 ml) and with 0.56 g of solid KOH.

The reaction mixture was heated for 2 h, then concentrated and filtered. The filtered solution was evaporated until the solid product was separated. After filtration and washing with petroleum ether, the product was dissolved in methanol and precipitated with ethyl ether.

$Co^{III}BAE(BA)_2Br$ (V). $CoBr_2 \cdot 6H_2O$ (3.3 g, 10 mmole) and 2.56 g (10 mmole) of BAE were dissolved in hot methanol. After addition of BA (4 ml) the reaction mixture was heated for 2 h and the product was precipitated with water, dissolved in hot acetone and reprecipitated by slow addition of petroleum ether (b.p. 30–50°).

$CH_3Co^{III}BAE \cdot H_2O$ (VII). $CoBAE(NH_3)_2Cl$ (3.6 g, 10 mmole) was suspended in 30 ml anhydrous THF and treated dropwise under stirring at 0° with 10 ml of Grignard reagent (3 *M*) prepared from CH_3Br and Mg in THF. The temperature was allowed to raise under stirring and after 3 h the reaction mixture was poured in ice-cooled water and hydrolized with an excess of HCl (2 *N*). By concentration of the red solution and neutralization with aqueous ammonia eventually a red crystalline solid was obtained, air dried.

The product was purified three times by dissolution in aqueous HCl and precipitation with ammonia. The same compound was obtained also starting from the complexes (III) to (VI) following the same procedure described above, except that when (VI) was starting complex only 1.5 mole of Grignard reagent per mole of (VI) was used. The rough product was washed with petroleum ether.

$C_2H_5Co^{III}BAE \cdot H_2O$ (VIII) was prepared exactly as described for the CH_3Co-$BAE \cdot H_2O$ using the corresponding Grignard reagent. Even in this case the product can be obtained starting from complexes (III) to (VI).

$C_6H_5Co^{III}BAE \cdot H_2O$ (IX) was prepared in the same way as the corresponding alkyl derivatives using corresponding Grignard reagent. The rough product was washed with petroleum ether until all the biphenyl was eliminated. The same product was obtained also starting from the complexes (III) to (VI).

In the preparation from C_6H_5Li 2.4 g (5 mmole) of $CoBAE(PPh_3)Br$ dissolved in anhydrous ether were reacted with the stoichiometric amount of C_6H_5Li in ether for 6 h under stirring. The separated red product was washed with ether under nitrogen. From the washing ether the PPh_3 displaced from the complex was recovered (m.p. 78–79°). The product was then dissolved in aqueous acid and precipitated with ammonia. The reaction mixture was hydrolized and neutralized. The same product (IX) was obtained also starting from complexes (II)–(V) and using the same procedure described above.

$CH_3Co^{III}(BAE)$ (X) was prepared by heating (VII) at 100° for 2 h under vacuum. The colour changes from red to green and the crystalline solid becomes a green powder. Recrystallization from anhydrous benzene yielded green needles.

$C_2H_5Co^{III}(BAE)$ (XI) was prepared from (VIII) by careful heating under vacuum at 60°. A green powder was obtained which was not recrystallized.

$C_6H_5Co^{III}BAE$ (XII) was prepared from (IX) by heating at 100° under vacuum. The green powder was not recrystallized.

$C_6H_5Co^{III}BAE(Py)$ (XIII) was prepared dissolving (XII) in ethyl ether and adding a slight excess of pyridine. The solution becomes orange and a red crystalline product was precipitated.

Reduction of (X) with $NaBH_4$

(X) (1 g) was dissolved in deaerated methanol/water and treated with a slight excess of $NaBH_4$. After some time the solution becomes deep yellow and by concentration under vacuum the crystalline yellow $Co^{II}BAE$, m.p. 151–152°, was obtained in good yield. From the latter the $Co^{III}BAE(NH_3)_2Cl$ was obtained by reaction with concd. NH_3, NH_4Cl and the calcd. amount of H_2O_2[1].

UV and visible spectra

These were obtained using a Unicam SP 700 spectrophotometer and 0.1; 1 and 10 cm silica cells. The solvent used was 95 % ethanol for the complexes $Co(BAE)L_2X$, $Co(BAE)LX$ and $Co^{II}BAE$ as well as for BAE. The green RCoBAE complexes were examined in benzene solution.

Magnetic measurements

These were carried out adopting the Faraday method.

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SUMMARY

The preparations of the complexes $Co^{II}(BAE)$, $[Co^{III}(BAE)L_2]X$, $Co^{III}(BAE)LX$ and of some new stable organocobalt complexes $RCo^{III}(BAE)$ and $RCo^{III}(BAE)\cdot H_2O$ are described (BAE = bis(acetylacetone) ethylendiamine; L = NH_3, $C_6H_5CH_2NH_2$, C_6H_5N, $(C_6H_5)_3P$; X = Cl, Br). The UV and visible absorption spectra are reported. The compounds RCo(BAE) appear to be new examples of penta-coordinated organocobalt complexes and constitute further evidence for the stabilization of the cobalt–carbon bond by chelation. The labilization of the sixth ligand by the alkyl or aryl group in the *trans* position is pointed out.

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