

REDUCTION OF COBALT CHELATES OF BIS(ACETYLACETONE)-ETHYLENEDIIMINE AND SYNTHESIS OF ORGANOCOBALT DERIVATIVES

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INTRODUCTION

A new series of stable organocobalt chelates with tetradentate ligand systems, bis(acetylaceton)ethylenediiminato dianion (BAE): $[\text{RCo}(\text{BAE})]$ or $[\text{RCo}(\text{BAE})\text{L}]^1$ and bis(salicylaldehyde)ethylenediiminato dianion (salen): $[\text{RCo}(\text{salen})]$ or $[\text{RCo}(\text{salen})\text{L}]^2$ (R = alkyl, aryl; L = Lewis base) were recently obtained by the Grignard reaction from the complexes, $[\text{XCo}^{\text{III}}(\text{BAE})\text{L}]$ or $[\text{Co}^{\text{III}}(\text{BAE})\text{L}_2]\text{X}$, and $[\text{XCo}^{\text{III}}(\text{salen})\text{L}]$ or $[\text{Co}^{\text{III}}(\text{salen})\text{L}_2]\text{X}$, respectively.

The results of electrochemical³ and photochemical⁴ investigations confirm that the above complexes can be considered as model molecules for the Vitamin B₁₂ group.

Stabilization of the cobalt-carbon bond was previously observed in the "cobaloximes" $[\text{RCo}(\text{DH})_2\text{L}]$, containing the bis-bidentate ligand system bis-dimethylglyoximato dianion (DH)₂, which were proposed as model molecules for the alkylcobalamins⁵.

In analogy with the alkylcobalamins⁶ and alkyl porphyrins⁷, the cobaloximes can be obtained also by reaction of the appropriate electrophilic reagent with the reduction product of the parent complexes, $[\text{Co}^{\text{III}}(\text{DH})_2\text{LL}]^8$. The reduction products were formulated as Co^I derivatives.

The present paper reports on the reduction of the chelates of (BAE) and the preparation of several new organometallic derivatives, including binuclear complexes, from the reduction products.

RESULTS

(1) The reaction of $[\text{BrCo}^{\text{III}}(\text{BAE})\text{PPh}_3]$ or $[\text{Co}^{\text{III}}(\text{BAE})]$ with sodium or 1% sodium amalgam in anhydrous tetrahydrofuran (THF) produces a deep green solution. When benzene or diethylether is used as solvent, the violet solid, $\text{NaCo}(\text{BAE})$ (I), is precipitated. The complex is highly sensitive to air and moisture but is stable at room temperature in an inert atmosphere. Solutions of (I) in THF react with de-aerated water in an inert atmosphere forming deep red solutions which gradually discolour yielding eventually yellow solutions of $[\text{Co}^{\text{II}}(\text{BAE})]$ with evolution of H₂. The transient formation of $\text{HCo}(\text{BAE})$ (II) is postulated, followed by reoxidation. The de-

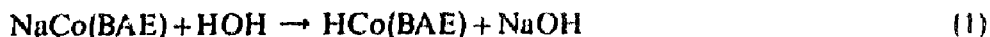


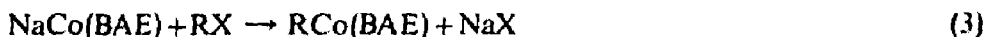
TABLE I
ANALYSES (%) AND MELTING POINTS OF (BAE) COMPLEXES OF COBALT^{III}

No.	Formula	C		H		N		M.p.	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(V)	n-C ₃ H ₇ Co(BAE)H ₂ O	52.63	52.11	7.95	8.08	8.18	8.32	113	red crystals from acetone/water
(VI)	Br(CH ₂) ₄ Co(BAE)H ₂ O	44.14	44.32	6.48	6.47	6.43	6.42	139	red crystals from acetone/water
(VII)	CH ₃ COCo(BAE)	51.85	52.10	6.53	6.77	8.64	8.65	142	violet crystals from benzene
(VIII)	CH ₂ =CHCo(BAE)H ₂ O	51.53	52.20	7.10	7.38	8.58	8.63	112	orange-red crystals from acetone/water
(IX)	CNCH ₂ CH ₂ Co(BAE)	53.73	53.90	6.61	6.83	12.53	12.61	149	red crystals from acetone/water
(X)	n-C ₃ H ₇ Co(BAE)	55.55	55.88	7.77	7.91	8.64	8.77	113	green crystals
(XI)	Br(CH ₂) ₄ Co(BAE)	46.05	45.88	6.28	6.17	6.72	6.81	139	green crystals
(XII)	CH ₂ =CHCo(BAE)	54.54	53.77	6.87	7.05	9.08	9.20	112	blue-violet crystals
(XIII)	Co(BAE)(CH ₂) ₄ Co(BAE)	54.36	54.44	7.17	7.43	9.06	9.02	162	green crystals from CH ₂ Cl ₂
(XIV)	CH ₃ Co(BAE)C ₃ H ₇ N	57.60	57.65	6.98	6.72	11.20	11.05	193-4	red crystals
(XV)	CH ₃ COCo(BAE)C ₃ H ₇ N	56.57	56.53	6.50	6.69	10.42	10.39	112	red crystals
(XVI)	CH ₂ =CHCo(BAE)C ₃ H ₇ N	58.90	59.45	6.76	6.73	10.85	10.76	149-50	red crystals
(XVII)	CNCH ₂ CH ₂ Co(BAE)C ₃ H ₇ N	57.96	57.82	6.56	6.43	13.52	13.33	159	red crystals
(XVIII)	CH ₃ Co(BAE)C ₆ H ₅ N ₂	57.96	58.10	6.57	6.82	13.52	13.80	193 dec.	red crystals
(XIX)	C ₆ H ₅ Co(BAE)C ₆ H ₅ N ₂	63.02	63.54	6.14	6.47	11.76	11.85	224	red crystals
(XX)	C ₆ H ₅ Co(BAE)C ₆ H ₉ N	64.50	64.89	6.93	6.72	9.11	9.23	183	orange-yellow crystals
(XXI)	[CH ₃ Co(BAE)] ₂ C ₂ H ₄ (NH ₂) ₂	51.53	51.62	7.72	8.01	12.87	13.07	195-7	orange-red crystals
(XXII)	[C ₆ H ₅ Co(BAE)] ₂ C ₂ H ₄ (NH ₂) ₂	58.75	58.35	7.00	7.24	10.82	10.96	236-7	orange-yellow crystals
(XXIII)	[C ₆ H ₅ Co(BAE)] ₂ C ₄ H ₁₀ N ₂	59.84	60.01	7.03	6.48	10.47	10.60	242	orange-red crystals



composition of (II) can be followed by measurement of the H_2 evolved. The results are in agreement with reactions (1) and (2). Both (I) and (II) can be formulated as Co^I derivatives.

(2) Solutions of either (I) or (II) in THF can be used as starting materials (containing the powerful nucleophilic species, $\text{NaCo}^I(\text{BAE})$ or $\text{HCo}^I(\text{BAE})$, respectively) for the preparation of a variety of stable organometallic derivatives by reaction with the appropriate electrophilic reagents, R-X ($\text{X} = \text{Cl, Br, I}$) followed by precipitation with H_2O .

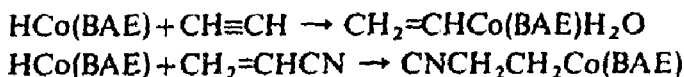


The products (see Table 1) are either the orange-red crystalline six-coordinated complexes $[\text{RCo(BAE)H}_2\text{O}]$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, \text{Br}(\text{CH}_2)_4; \text{CH}_2=\text{CH}$), or the apparently five-coordinated $[\text{RCoBAE}]$ ($\text{R} = \text{CH}_3\text{CO}$; violet crystals). The methyl and ethyl derivatives are identical with those previously reported¹ by Grignard reaction.

All the compounds can be obtained as five-coordinated complexes from non-coordinating solvents (benzene, CH_2Cl_2 etc.) or by heating $[\text{RCo(BAE)H}_2\text{O}]$ in the solid state under vacuum.

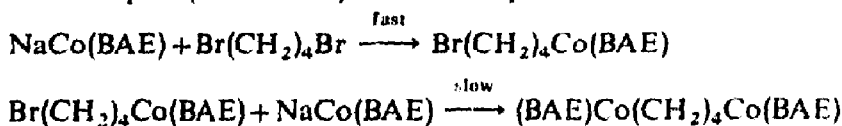
In contrast to the corresponding complex of salen^9 , the carboxyalkyl derivatives ($\text{R} = \text{CH}_3\text{OCO}$) could not be obtained by reaction (3). The phenyl derivatives, $[\text{C}_6\text{H}_5\text{Co(BAE)}]$ and $[\text{C}_6\text{H}_5\text{Co(BAE)H}_2\text{O}]$, could not be obtained by the above reaction, but were prepared as stable products by the Grignard reaction from $[\text{XCo(BAE)L}]^1$.

(3) Unsaturated compounds such as acetylene or activated vinyl derivatives react with THF solutions of (II) with formation of stable red crystalline addition products (see Table 1).

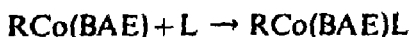


The same complexes are obtained when solutions of (I) in THF are reacted with water in the presence of unsaturated compounds.

(4) Treatment of (I) with the aliphatic geminal dihalide, $\text{Br}(\text{CH}_2)_4\text{Br}$, afforded a binuclear complex (see Table 1) in a two-step reaction.



(5) The five-coordinated species, $[\text{RCo(BAE)}]$, are easily converted into the six-coordinated $[\text{RCo(BAE)L}]$ by addition of the appropriate Lewis base ($\text{L} = \text{pyridine, benzylamine, benzimidazole}$) (see Table 1).



From $[\text{RCo(BAE)H}_2\text{O}]$, the coordinated water can be displaced by excess of various ligands.



(6) Bifunctional donor molecules (*e.g.*, ethylenediamine, piperazine) can be used as bridging ligands to obtain binuclear complexes (see Table 1).



The orange-red crystalline products are stable in the solid state but easily dissociate in non-complexing solvents, yielding $[\text{RCo}(\text{BAE})]$.

(7) The complexes $[\text{XCo}^{\text{III}}(\text{BAE})\text{L}]$ or $[\text{Co}^{\text{III}}(\text{BAE})\text{L}_2]\text{X}$ can be reduced also by NaBH_4 but give $[\text{Co}^{\text{II}}(\text{BAE})]$ as the final reaction product. In the presence of CH_3I , the methyl-cobalt derivative, $[\text{CH}_3\text{Co}(\text{BAE})]$, is obtained. The intermediate formation of the Co^{I} species can be assumed.

DISCUSSION

Relatively unstable organometallic cobalt complexes were previously prepared using σ -donor- π -acceptor ligands such as PR_3 ¹⁰, CO ¹¹, CN^- ¹²; deeply coloured Co^{I} complexes were reported with ligands, such as 2,2'-bipyridyl¹³, *o,o'*-phenanthroline¹ and $\text{C}_2\text{H}_4(\text{PPh}_2)_2$ ¹⁵, stabilizing low-valence states of transition-metal atoms.

On the other hand, naturally occurring ligands such as the porphyrin and corrin macrocycles afford both the low-valence state (Vitamin B_{12}) and very effective cobalt-carbon bond stabilization (alkyl cobalamins).

Both properties are thus essential requirements for ligands used to obtain model complexes for the Vitamin B_{12} group compounds *e.g.*, the bis-dimethylglyoximatocobalt complexes reported and investigated by Schrauzer.

The present work and the following paper⁹ demonstrate that other chelating agents such as (BAE) and (salen) impart very similar properties. We can thus arrange for different series of comparatively simple cobalt chelates the physico-chemical behaviour of which can be investigated in order to correlate the electronic and structural features of the planar ligand with the coordination chemistry of the cobalt atom and properties of the cobalt-axial ligands bonds.

The most important common feature is, in our opinion, the conjugation in the planar ligand system involving the *d*-electrons of the cobalt atom.

As far as the chemical behaviour is concerned, some differences are apparent such as the behaviour towards reduction with NaBH_4 . While the cobaloximes are reduced to Co^{I} derivatives⁵, the corresponding complexes of (BAE) are reduced to $[\text{Co}^{\text{II}}(\text{BAE})]$. The intermediate formation of very unstable Co^{I} complexes can be assumed.

Much more detailed information on the redox mechanism and stability of reduced species is obtained from electrochemical investigations³.

Moreover, the stability of the carboxyalkyl derivatives of (BAE) are also distinctly lower than in the cobaloximes or salen⁴ series.

In the $[\text{RCo}(\text{BAE})\text{L}]$ complexes, the lability of the Co-L bond is influenced both by the presence of the planar and the nature of the *trans*-(axial) ligand (*cis*- and *trans*-effect). The transmission of electronic effects through the cobalt atom has been studied by NMR¹⁶ and spectroscopical³ methods.

The reduction mechanism and the oxidation state of the cobalt atom is briefly discussed in the following paper⁹.

EXPERIMENTAL

NaCo(BAE) (I)

[Co^{II}(BAE)] (2.81 g, 10 mmole) dissolved in anhydrous THF was reduced with excess Na or 1% Na(Hg) in an inert atmosphere. A suspension of a violet solid in a green solution was obtained. The solid product (impure NaCo(BAE)) was filtered and the solution evaporated to dryness under vacuum, at room temperature. When anhydrous ether or benzene was used, a violet solid in a colourless solution was obtained.

Reaction of (I) with water. A THF solution of (I) treated with de-aerated water in an inert atmosphere became reddish-brown in colour. The solution slowly discoloured to yellow. On evaporation, crystalline, yellow [Co^{II}(BAE)] was obtained (comparison with authentic sample by IR spectrum; m.p. and mixed m.p. 151-2°).

When 1 mmole of (I) in anhydrous THF (150 ml) was treated with 5 ml of de-aerated water (23°), 12.5 ml of H₂ (S.T.P.) was evolved after 11 min (calcd. for HCo(BAE), 11.2 ml).

[RCo(BAE)H₂O] (R = CH₃, (III), C₂H₅ (IV), n-C₃H₇ (V), Br(CH₂)₄ (VI))

[Co^{II}(BAE)] (2.81 g, 10 mmole), dissolved in anhydrous THF (200 ml) was reduced in an inert atmosphere with 1% Na(Hg). The amalgam was withdrawn and the solution cooled (-80°) and treated with the stoichiometric amount of the appropriate alkyl halide RX (X = Br, I). The reaction mixture was poured into water (100 ml). After evaporation, red crystals separated (70% yield). When recrystallized from acetone-water, (III) and (IV) were identical with those previously obtained from Grignard reagents¹.

(III) can also be obtained by reduction of [Co(BAE)(NH₃)₂]Cl or [BrCo(BAE)PPh₃] with NaBH₄ (ethanol-water solution in an inert atmosphere in the presence of CH₃I). The compound was isolated and purified as above (40% yield).

[CH₃COC₂Co(BAE)] (VII)

Obtained from a cooled (-80°) solution of (I) by reaction with the stoichiometric amount of CH₃COCl or (CH₃CO)₂O.

The deep violet crystalline compound was isolated as above and recrystallized from benzene (65% yield). IR carbonyl absorption (CH₂Cl₂ solution) $\nu(\text{C}=\text{O}) = 1720 \text{ cm}^{-1}$.

When ClCOOCH₃ or ClCH₂COOCH₃ was used as the reagent, [Co^{II}(BAE)] was recovered quantitatively.

[CH₂=CHCo(BAE)] (VIII)

Obtained (a) by treatment of a THF solution of (I) with CH₂=CHCl as above (50% yield); (b) by reaction of a THF solution of (I) with water, followed by the addition of CH₂=CHCl (low yield); (c) by the addition of water to a THF solution of (I) saturated with acetylene; (d) by reaction of a THF solution of (I) with de-aerated water followed by saturation with acetylene.

All the above procedures give the same crystalline compound (IR spectra, m.p. and mixed m.p. 112°), (70% yield).

TABLE 2
NEAR ULTRAVIOLET AND VISIBLE ABSORPTION FREQUENCIES AND INTENSITIES OF (BAE) COMPLEXES OF COBALT
Frequencies of absorption bands revealed as shoulders are estimated; intensities are given for the absorptions at the estimated frequency of the underlying band.

Formula	Frequencies ($\text{cm}^{-1} \cdot 10^{-3}$) and $\log \epsilon_{\text{max}}$ (in brackets)			Solvent
NaCo(BAE)	26.4	24.6 sh	14.9	THF
Br(CH ₂) ₂ Co(BAE)	25.9 sh (3.40)		14.7 (2.56)	CH ₂ Cl ₂
CNCH ₂ CH ₂ Co(BAE)	26.8 sh (3.45)		14.4 (2.80)	CH ₂ Cl ₂
CNCH ₂ CH ₂ Co(BAE)C ₃ H ₅ N	27.1 sh (3.61)	25.0 sh (3.46)	19.9 (2.74)	EtOH/C ₃ H ₅ N
n-C ₃ H ₇ Co(BAE)	26.8 sh (3.40)		14.8 (3.07)	CH ₂ Cl ₂
n-C ₃ H ₇ Co(BAE)C ₃ H ₅ N	25.9 sh (3.51)	24.4 sh (3.39)	19.8 (2.76)	EtOH/C ₃ H ₅ N
CH ₃ COCo(BAE)			17.4 (2.87)	CH ₂ Cl ₂
CH ₃ COCO(BAE)C ₃ H ₅ N	28.0 sh (3.59)		21.5 (2.83)	EtOH/C ₃ H ₅ N
CH ₂ =CHCo(BAE)	28.4 sh (3.74)		16.0 (2.86)	CH ₂ Cl ₂
CH ₂ =CHCo(BAE)C ₃ H ₅ N			20.6 (2.76)	EtOH/C ₃ H ₅ N
Co(BAE)(CH ₃) ₂ Co(BAE)	28.6 sh (4.02)	25.4 sh (3.51)	14.6 (3.10)	CH ₂ Cl ₂
[(CH ₂) ₂ Co(BAE)C ₃ H ₅ N] ₂	29.2 sh (4.09)	23.95 sh (3.51)		
	26.0 sh (3.79)	24.3 sh (3.62)	20.1 (3.05)	EtOH/C ₃ H ₅ N

$[CNCH_2CH_2Co(BAE)]$ (IX)

Obtained by procedures (b) and (c) above using $CH_2=CHCN$ as reagent. Purple crystals from acetone-water (80% yield).

 $[RCo(BAE)]$ ($R = C_3H_7$ (X), $Br(CH_2)_4$ (XI), $CH_2=CH$ (XII))

Obtained by heating (40–80°) the *aquo*-derivatives in the solid state under vacuum. The compounds are green, with exception of the vinyl derivative which is deep violet. The same compounds are obtained (IR spectra) from the *aquo*-derivatives in C_6H_6 , $CHCl_3$, CH_2Cl_2 (100% yield).

 $[(BAE)Co(CH_2)_4Co(BAE)]$ (XIII)

Obtained by reacting a THF solution of (I) with the stoichiometric amount of (XI). The green solution was treated with water and concentrated under vacuum. The green, crystalline solid was washed with acetone and recrystallized from CH_2Cl_2 (70% yield).

 $[RCo(BAE)C_5H_5N]$ ($R = CH_3$ (XIV), CH_3CO (XV), $CH_2=CH$ (XVI), $CNCH_2CH_2$ (XVII))

Obtained by dissolving the five-coordinated complexes, $[RCo(BAE)]$ or $[RCo(BAE)H_2O]$, in the minimum amount of pyridine, and precipitating with petroleum ether (90% yield). When $R = C_2H_5$ or C_3H_7 , the six-coordinated pyridinates can be formed only in a solution containing excess of pyridine. Loss of pyridine takes place during isolation of the solid product. $\nu(CO)(XV) = 1692\text{ cm}^{-1}$ (ethanol-pyridine solution).

 $[RCo(BAE)C_7H_6N_2]$ ($R = CH_3$ (XVIII), C_6H_5 (XIX))

Obtained by the addition of benzimidazole (saturated ethanolic solution) to the corresponding five-coordinated or six-coordinated *aquo*-complexes in alcohol. Washed with a little ethanol (80% yield).

 $[C_6H_5Co(BAE)C_7H_9N]$ (XX)

Obtained as orange-yellow crystals from $[C_6H_5Co(BAE)]$ or $[C_6H_5Co(BAE)H_2O]^+$ by treatment with benzylamine in ethanol. Washed with water-ethanol (60% yield).

 $[[RCo(BAE)NH_2CH_2)_2]$ ($R = CH_3$ (XXI), C_6H_5 (XXII))

Obtained by heating an ethanolic solution of $[RCo(BAE)]$ or $[RCo(BAE)H_2O]^+$ with ethylenediamine. An orange-red crystalline solid separated on cooling and was thoroughly washed with water (80% yield).

 $[(C_6H_5Co(BAE))_2C_4H_{10}N_2]$ (XXIII)

Obtained by the addition of $C_4H_{10}N_2$ to $[C_6H_5Co(BAE)]$ in ethanol. On standing an orange-yellow crystalline compound was formed and was filtered and washed with ethanol (60% yield).

Spectra

The spectral data of (BAE) complexes of Co^{III} are given in Table 2. The UV and

visible spectra were determined using an Unicam SP 700 spectrophotometer. During all the operations, care was taken to avoid photochemical decomposition.

Infrared spectra were obtained with KBr pellets using a Perkin-Elmer model ^{13}C infrared spectrophotometer.

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SUMMARY

Complexes of Co^{III} and Co^{II} of the type $\text{BrCo}(\text{BAE})\text{PPh}_3$ or $\text{Co}^{\text{II}}(\text{BAE})$ can be reduced to $\text{NaCo}^{\text{I}}(\text{BAE})$ by Na or 1% Na(Hg).

The preparation of stable organocobalt complexes, $\text{RCo}(\text{BAE})$ and $\text{RCo}(\text{BAE})\text{H}_2\text{O}$ (R = alkyl, vinyl, acyl), by reaction of $\text{NaCo}^{\text{I}}(\text{BAE})$ with RX, is described.

Six-coordinated complexes, $\text{RCo}(\text{BAE})\text{L}$ (L = pyridine, benzylamine, benzimidazole) were also prepared.

The reactions of $\text{NaCo}^{\text{I}}(\text{BAE})$ with acetylene and acrylonitrile in the presence of water yielding the vinyl and cyanoethyl derivatives are reported.

Binuclear complexes $(\text{BAE})\text{Co}(\text{CH}_2)_4\text{Co}(\text{BAE})$ and $[\text{RCo}(\text{BAE})\text{NH}_2\text{CH}_2]_2$ are also obtained.

The chemical behaviour of the Co^{I} complex shows a strong analogy with that of the Vitamin B_{12} .

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