ORGANOMETALLIC DERIVATIVES OF COBALT(III) CHELATES OF BIS(SALICYLALDEHYDE) ETHYLENEDIIMINE

G. COSTA, G. MESTRONI AND L. STEFANI

Institute of Chemistry, University of Trieste, Trieste (Italy)

(Received June 26th, 1966)

In a previous paper[1] we described some novel stable derivatives of Co(III) chelates of bis(acetylacetone) ethylenediimine (BAEH$_2$)* containing an alkyl– or aryl–cobalt σ-bond. The relevance of this type of compounds, as well as that of cobaloximes[2], to the investigations of alkylcobalamins model molecules[2-4] prompted us to attempt the preparation of organometallic derivatives of other cobalt chelates in order to provide further information on the influence of chelation on the physico-chemical properties and reactivity of these complexes, with particular attention to the cobalt–carbon bond.

We wish to report in the present work some novel organometallic cobalt chelates of bis(salicylaldehyde) ethylenediimine (salen H$_2$).

The oxygen-carrying complex of the tetradentate Schiff's base Co^{II}(salen)[5] has been extensively studied[6,7]. Only recently the hexacoordinated complexes of the type [Co(salen)L$_2$]$^+$X$^-$ (L = NH$_3$, CH$_3$NH$_2$, C$_2$H$_5$NH$_2$, C$_3$H$_7$NH$_2$, C$_4$H$_9$NH$_2$, C$_5$H$_5$N, H$_2$O; X$^-$ = Cl$^-$, ClO$_4^-$) and [Co(salen)L$_2$]$^-$K$^+$ (L = NO$_2^-$, CN$^-$) (see structure A) were described[8].

(A)
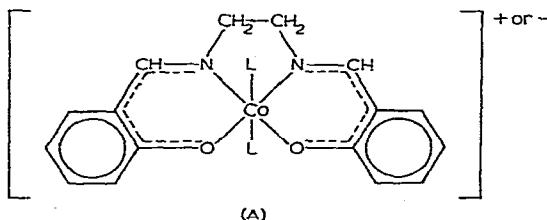
A square planar structure was assigned[9] to the [Co^{II}(salen)], the mono-nitrosyl is supposed to be a pentacoordinated species with square pyramidal structure[10] and the hexacoordinated complexes are probably distorted octahedral. The latter were choosen as starting substances for the preparation of organometallic derivatives.

RESULTS

For the present investigation the complexes [Co(salen)L$_2$]$^+$Br$^-$ [L = NH$_3$ (I), pyridine (II), benzylamine, (III)] and [Co(salen)(PPh$_3$)Br] (IV) were prepared.

---

* The symbol (BAEH$_2$) is more correct for bis(acetylacetone) ethylenediimine instead of BAE used in the previous paper[1].

TABLE 1

ANALYSES (%) AND MELTING POINTS OF (salen) COMPLEXES OF COBALT (III)

No.	Formula[a]	C: found	calcd.	H: found	calcd.	N: found	calcd.	Co: found	calcd.	M.p.
(I)	Co(salen)(NH₃)₂Br·H₂O	42.02	42.03	5.05	4.85	12.26	12.26	12.73	12.89	249–50°
(II)	Co(salen)(C₅H₅N)₂Br·H₂O	53.17	53.71	4.93	4.50	9.55	9.64	9.8	10.13	252°
(III)	Co(salen)(H₂NCH₂C₆H₅)₂Br	58.17	58.17	5.49	5.21	9.07	9.05	9.37	9.52	290°
(IV)	Co(salen)PPh₃Br	61.29	61.18	4.42	4.38	4.15	4.19	8.84	8.83	151–2°
(V)	CH₃Co(salen)·H₂O	57.11	56.98	5.62	5.35	7.99	7.82	16.19	16.45	150° (dec.)
(VI)	C₃H₇Co(salen)·H₂O	59.61	59.07	6.16	6.00	7.20	7.25	15.10	15.25	150°
(VII)	C₄H₉Co(salen)·H₂O	59.78	59.99	7.25	6.28	6.96	6.99	14.58	14.72	150°
(VIII)	C₆H₅Co(salen)·H₂O	62.87	62.87	5.40	5.04	6.45	6.66	13.81	14.02	>300° (dec.)
(IX)	C₂H₅Co(salen)	60.66	61.01	5.59	5.40	7.78	7.90	16.44	16.63	150° (dec.)
(X)	CH₃Co(salen)	59.64	59.99	5.31	5.04	8.36	8.23	17.15	17.32	150°
(XI)	CH₃Co(salen)NH₃	57.12	57.14	5.70	5.64	11.60	11.76	16.31	16.50	150° (dec.)
(XII)	C₆H₅Co(salen)NH₃	62.95	63.02	5.38	5.29	10.20	10.02	13.85	14.06	>300° (dec.)
(XIII)	CH₃Co(salen)C₇H₆N₂	62.82	63.02	5.36	4.85	12.28	12.25	12.84	12.89	150° (dec.)
(XIV)	CH₃Co(salen)C₅H₅N	63.42	63.01	5.11	5.29	10.14	10.02	13.84	14.05	150°
(XV)	C₂H₅Co(salen)C₅H₅N	63.19	63.73	6.30	5.58	9.78	9.69	13.31	13.59	150°
(XVI)	C₃H₇Co(salen)C₅H₅N	64.11	64.42	6.07	5.86	9.30	9.39	13.02	13.17	150°
(XVII)	C₄H₉Co(salen)C₅H₅N	66.37	65.93	6.22	6.19	9.27	9.23	12.78	12.94	150°
(XVIII)	C₆H₅Co(salen)C₅H₅N	67.53	67.36	5.27	5.03	8.48	8.73	11.95	12.24	290°
(XIX)	C₆H₅Co(salen)	65.24	65.67	4.93	4.76	7.19	6.96	14.38	14.65	>300° (dec.)
(XX)	Co(salen)(CN)₂K	51.84	51.92	3.36	3.44	13.66	13.77	14.01	14.13	>300° (dec.)

[a] (salen) = bis(salicylaldehyde) ethylenediiminato, $-O-o-C_6H_4CH=NCH_2CH_2N=CHC_6H_4-o-O-$; C_5H_5N = pyridine; $C_7H_6N_2$ = benzimidazole.

Treatment of (I)-(IV) with the appropriate Grignard reagent in THF gave the complexes [RCo(salen)·H₂O] [R = CH₃ (V), C₃H₇ (VI), C₄H₉ (VII), C₆H₅ (VIII)] as stable orange-yellow crystalline compounds. As the only exception the reaction of ethylmagnesium bromide with (I)–(IV) yields [C₂H₅Co(salen)], (IX), directly as a deep red crystalline solid. The IR spectrum confirms the absence of a coordinated water molecule in this compound. All the above organometallic derivatives, as well as the parent complexes, are diamagnetic. Analyses and m.p.'s are reported in Table 1.

The complexes (V)–(IX) are stable in the solid state, insoluble in water, but soluble in aqueous acids, methanol, ethanol, N,N-dimethylformamide, dimethyl sulphoxide, pyridine giving yellow to red solutions. The solubility decreases with changes of R in the following order: CH₃ > C₂H₅ > C₃H₇ > C₄H₉ > C₆H₅. In acetone, chloroform, methylene chloride and benzene all the complexes are soluble or slightly soluble, and give green solutions.

From the green solution of (V) in CH₂Cl₂ a complex consistent with formula [CH₃CO(salen)], (X), can be crystallized as deep red crystals. From the green CH₂Cl₂ solutions of (IX) and (VIII), the deaquated form (IX), or the aquocomplexes, (VIII), are reobtained by crystallization.

By treatment of (V)–(VIII) with the appropriate base the complexes RCo-(salen) L (L = NH₃, pyridine, benzimidazole) are obtained (see Table 1).

UV and visible absorption frequencies and intensities are reported in Table 2.

From [RCo(salen)L] the ligand L(H₂O, NH₃, pyridine) is displaced by heating. Increasing rates were observed as R was changed in the order C₆H₅ < CH₃ < C₄H₉ ~ C₃H₇ < C₂H₅.

By thermal decomposition at higher temperature even the alkyl radical directly bound to the cobalt atom is cleaved and quantitative yield of [Co^II(salen)] was eventually observed.

When the phenyl derivatives (VIII), (XII), and (XVIII) are heated just under the m.p. they give only the green solid [C₆H₅Co(salen)].

Solutions of [RCo(salen)L] in ethanol/water, pyridine/water or methylene chloride were found to be photolabile.

In aqueous concentrated acids the complexes are slowly hydrolyzed in the dark to give Co^++ and the hydrolysis products of the bis(salicylaldehyde) ethylene-diimine ligand. The reaction is remarkably accelerated by the light.

In the presence of CN⁻ (in ethanol/water), [CH₃Co(salen)·H₂O] undergoes both cleavage of the cobalt–carbon bond and substitution of H₂O ligand yielding [Co(salen)(CN)₂]K, (XX), which was identified through UV and IR spectra.

DISCUSSION

From above results the similarity between the *course of the reaction* of hexa-coordinated chelate complexes of Co^III with (BAE)[1] and (salen) with Grignard reagents in THF can be pointed out.

The products are assumed to be σ-bonded organometallic derivatives containing the chelate rings in the x–y plane, the alkyl (or aryl) group and a sixth ligand (when present) on the z axis in the trans position. Planarity of the chelate rings in square planar complexes of Co^II, Cu^II and Zn^II with (salen) was indeed determined from X-ray data[10–13]. If the ligands are considered as anions the above complexes

G. COSTA, G. MESTRONI, L. STEFANI

TABLE 2

ULTRAVIOLET AND VISIBLE ABSORPTION FREQUENCIES AND INTENSITIES OF (salen) COMPLEXES OF COBALT (III)

Frequencies of absorption bands revealed as shoulders are estimated; intensities are given for the absorption curve at the estimated frequency of the underlying band.

Formula[a]	Frequencies ($cm^{-1} \times 10^{-3}$) and $\log \varepsilon_{max}$ (in brackets)					Solvent
$Co(salen)$	28.6 (3.95)	24.5 (4.02)	21.0 sh (3.37)			CH_2Cl_2
$CH_3Co(salen)H_2O$	29.2 (4.21)	25.4 sh (3.79)	22.0 sh (3.42)		15.35 (3.15)	CH_2Cl_2
$CH_3Co(salen)C_5H_5N$	28.4 (3.94)	25.4 sh (3.76)	22.7 sh (3.57)	20.4 sh (3.37)	15.3 (b)	EtOH/C_5H_5N
$C_6H_5Co(salen)H_2O$	28.8 (b)	25.8 sh (b)	22.4 sh (b)			CH_2Cl_2
$C_6H_5Co(salen)C_5H_5N$	28.4 (3.91)	24.8 sh (3.67)	23.5 sh (3.67)	20.7 sh (3.31)	15.1 (3.13)	EtOH/C_5H_5N
$C_2H_5Co(salen)$	29.2 (4.13)	25.0 sh (3.78)	21.6 sh (3.42)			CH_2Cl_2
$C_2H_5Co(salen)C_5H_5N$	27.9 (3.92)	24.8 sh (3.76)	22.0 sh (3.50)	19.7 sh (3.29)	15.1 (3.11)	EtOH/C_5H_5N
$C_3H_7Co(salen)H_2O$	29.2 (4.15)	24.7 sh (3.78)	21.5 sh (3.38)			CH_2Cl_2
$C_3H_7Co(salen)C_5H_5N$	27.9 (3.92)	25.0 sh (3.78)	22.0 sh (3.53)	19.7 sh (3.33)	15.1 (3.13)	EtOH/C_5H_5N
$C_4H_9Co(salen)H_2O$	29.0 (4.15)	25.0 sh (3.78)	21.7 sh (3.41)			CH_2Cl_2
$C_4H_9Co(salen)C_5H_5N$	27.9 (3.95)	25.0 sh (3.78)	22.1 sh (3.50)	19.7 sh (3.27)		EtOH/C_5H_5N
$C_2H_5Co(BAE)$	28.8 sh (3.62)	25.8 sh (3.40)	22.7 sh (3.06)			CH_2Cl_2
$C_2H_5Co(BAE)C_5H_5N$	obs	26.4 sh (3.57)	24.0 sh (3.35)	20.1 (2.75)	15.0 (2.79)	EtOH/C_5H_5N
$C_6H_5Co(BAE)$	obs	26.8 (3.60)				CH_2Cl_2
$C_6H_5Co(BAE)C_5H_5N$	28.6 sh (3.69)	25.6 sh (3.50)		20.4 (2.72)	15.4 (2.92)	EtOH/C_5H_5N

[a] See footnote of Table 1; (BAE) = bis(acetylaceton) ethylenediiminato, $-OC(CH_3)=CHC(CH_3)=NCH_2CH_2N=C(CH_3)CH=C(CH_3)O-$. [b] The spectrum of a saturated solution was taken; intensities were not calculated.

can be regarded as diamagnetic complexes of tervalent cobalt with a carbanion as ligand in analogy with the alkylcobalamines[14].

Complexes of Co^{III} with dimethylglyoxime [XCo(DH)$_2$L] (X = Cl, Br; L = py, PPh$_3$, NMe$_3$ etc.) react similarly with Grignard reagents yielding generally [RCo(DH)$_2$L] (R = CH$_3$, C$_2$H$_5$, C$_6$H$_5$, C$_6$H$_5$CH$_2$) as was reported by Schrauzer[2] but we observed that the ligand L is retained or displaced by H$_2$O on hydrolysis of the Grignard reaction solution, depending on the nature of R and of L[15].

From cobalt chelates of (BAE)[1] the aquo derivatives [RCo(BAE)·H$_2$O] are obtained but in one case at least [C$_2$H$_5$Co(BAE)·H$_2$O] the H$_2$O ligand is lost by standing in the dessicator (P$_2$O$_5$), yielding an apparently pentacoordinated species (monomeric in benzene): C$_2$H$_5$Co(BAE).

From chelates of (salen) either aquo complexes [RCo(salen)·H$_2$O] (R = CH$_3$, C$_2$H$_7$, C$_4$H$_9$, C$_6$H$_5$) and [RCo(salen)] (R = C$_2$H$_5$) are directly obtained from hydrolyzed Grignard reaction solution. Even from [CH$_3$Co(salen)·H$_2$O] the species [CH$_3$Co(salen)] can be easily obtained. There is, thus, increasing stabilization of the assumed pentacoordinated species on going from dimethylglyoximato to bis-(acetylacetone) ethylenediiminato and bis(salicylaldehyde) ethylenediiminato complexes of cobalt.

It appears that the above complexes are suited for the study of the *trans*-effect and for comparison with the results recently published[16-17] on the vitamin B$_{12}$.

Researches in this direction are in progress in this laboratory.

Photolability was also qualitatively observed. It represents a further connection between the physico-chemical behaviour of [RCo(BAE)L] and [RCo(salen)-L] and that of the corrinoids. It appears that the homolytical cleavage of cobalt–carbon bond is catalyzed by light, as was recently pointed out in alkylcobalamines[18-19].

The similarity of the *electronic structure* around the cobalt atom, implying the same conjugate rings in the organometallic complexes of both (BAE) and (salen) is reflected in the electronic spectra, some of which are compared in the Table 2. The absorption at 28,000–29,000 cm^{-1}, 24,500–26,000 cm^{-1}, 21,000–22,000 cm^{-1} and ~ 20,000 cm^{-1} (pyridinato derivatives) or at 15,000 cm^{-1} (aquo complexes and pentacoordinated species in CH$_2$Cl$_2$ solution) are likely to be due to the same transitions between levels formed both from metal and ligand orbitals, in both types of chelates.

The electronic structure of the assumed pentacoordinated species and that of species present in solutions of the aquocomplexes in methylene chloride or benzene can be empirically related to the absorption at ~ 15,000 cm^{-1} which is displaced to 19,000–20,000 cm^{-1} in the hexacoordinated species (*e.g.* [RCo(salen)C$_5$H$_5$N], see Table 2).

Crystal field theory predicts that the two bands arising from $^1T_{1g} \leftarrow {}^1A_{1g}$ (I) and $^1T_{2g} \leftarrow {}^1A_{1g}$(II) transitions in the octahedral complexes of Co^{III} having O_h point symmetry are splitted in the D_{4h} symmetry into two components ($^1E_g \leftarrow {}^1A_{1g}$, $^1A_{2g} \leftarrow {}^1A_{1g}$ from band I (Ia and Ib) and $^1B_{2g} \leftarrow {}^1A_{1g}$, $^1E_g \leftarrow {}^1A_{1g}$ from band II[20].

From extensive investigations[21] on spectra of hexacoordinated Cobalt(III) complexes of the type CoA$_5$B and *trans*- or *cis*-CoA$_4$B$_2$ it is known that two or three bands are frequently observed in the region from about 30,000 cm^{-1} to the lower energy side of the spectrum.

In the cis-isomers only a broadening of the I band is noticed. Actual splitting of the low energy band can be observed in the trans-isomers if the axial ligand is well separated from the equatorial ligands in the spectrochemical series[21a]. When three bands are present the first two absorption maxima occurring from about 15,000 to 20,000 cm^{-1} and from 20,000 to 21,000 cm^{-1} are assigned to Ia and Ib transitions respectively. The third absorption maximum which occurs from 24,000 to 30,000 cm^{-1} is assigned to the unresolved band II.

From the solution spectra and circular dichroism in trans-dichlorobis(propylenediamine)cobalt(III) cation[21a,22] four absorptions in the same region were assigned to the transitions arising from the splitting of I and II bands[22].

In the present complexes the symmetry cannot be higher than C_{2v} and both ^1E_g levels are predicted to split into two (B_2 and B_1).

Assuming a small splitting of the ^1E_g levels four transitions could be still expected and three of them are now symmetry allowed.

The occurrence of four strong absorptions between 30,000 and 15,000 cm^{-1} in the present complexes could be explained either by further decrease in symmetry (actual symmetry being C_2) and by vibronic coupling.

On the other hand mixing of metal and ligand orbitals should be important in the systems under study. We prefer to delay a more detailed discussion of the spectra until we have results of approximate molecular orbital calculations which are being attempted in this laboratory.

Stabilization of the cobalt–carbon bond results from the proper stereochemical arrangement of the tetradentate ligand (approximately in the x–y plane) and participation of electrons of the cobalt atom in the π orbitals of the conjugate system of chelate rings (metal–ligand donor π bonds).

The π electrons of the conjugate systems of ligands interacts more strongly with the p_z, d_{xz} and d_{yz} electrons of the metal giving π molecular orbitals while the d_{z^2}, d_{xy} and $d_{x^2-y^2}$ electrons are mainly involved in the metal to ligands σ bonds in the x–y plane[3].

As a consequence of the above interactions, the energy and overlapping of the appropriate orbitals of the metal on the z axis are properly adjusted to give stable σ-bonding molecular orbitals, with alkyl or aryl groups.

The existence of stable, apparently pentacoordinated species [RCoBAE] and [RCo(salen)] suggests that the influence of the sixth ligand on the z axis is not essential in the stabilization of the cobalt–carbon bond.

EXPERIMENTAL

Preparation of the chelates

[Co(salen)(NH$_3$)$_2$]Br·H$_2$O$^-$ (I). (SalenH$_2$)(5.4 g, 20 mmole) was dissolved in a hot methanolic solution (100 cc) of 6.5 g of CoBr$_2$·6 H$_2$O (20 mmole), and conc. aqueous ammonia (5 cc) was added dropwise and the solution heated for 2 h under stirring. After cooling, the solid product was filtered, crystallized from water/ethanol and air-dried at 100°.

[Co(salen)(C$_5$H$_5$N)$_2$]Br·H$_2$O (II). This compound was prepared from 5.4 g of (salenH$_2$), 10 cc of pyridine and 6.5 g of CoBr$_2$·6 H$_2$O dissolved in methanol (100cc). After 2 h heating in the presence of air, the solution was concentrated to about 20 cc

and then treated with 100–150 cc of water. The brown solid formed, dissolved in ethanol, was crystallized as dark brown needles after addition of ether.

$[Co(salen)(H_2NCH_2C_6H_5)_2]Br$ (III). Prepared as above and crystallized from water/methanol as red-brown plates.

$[Co(salen)(PPh_3)Br]$ (IV). PPh$_3$ (5.1 g) dissolved in ether (100 cc), 5.4 g of (salenH$_2$) and 1.12 g of solid KOH were added to 6.5 g of CoBr$_2$·6 H$_2$O in methanol (100 cc). After 3 h heating in air, the solution was concentrated. The dark-green solid obtained was filtered, washed with water, acetone and ether and recrystallized from anhydrous ethanol.

$[CH_3Co(salen)\cdot H_2O]$ (V), $[C_3H_7Co(salen)\cdot H_2O]$ (VI), $[C_4H_9Co(salen)\cdot H_2O]$ (VII) and $[C_6H_5Co(salen)\cdot H_2O]$ $(VIII)$. RMgBr (R = CH$_3$, C$_3$H$_7$, C$_4$H$_9$ or C$_6$H$_5$) (15 mmole) in tetrahydrofuran (THF) was added dropwise at $-60°$ to 5 mmoles of (I) suspended in 100 cc of THF. The reaction mixture was stirred at room temp. for 4 h, poured into cold water and neutralized with 2N HCl. THF was removed by distillation under vacuum. The solid obtained was then filtered. (V), (VI) and (VII) were dissolved in hot methanol and precipitated with water as orange-yellow crystals. (VIII) was dissolved in hot N,N-dimethylformamide and precipitated with steam (as crystals).

The products (V)–(VIII) were also obtained by the same procedure by reaction of (II), (III) and IV with Grignard reagent.

$[C_2H_5Co(salen)]$ (IX). Prepared as above from (I)–(IV), recrystallized from an ethanolic solution by addition of water or from CH$_2$Cl$_2$.

$[CH_3Co(salen)]$ (X). Obtained as dark red crystals by concentrating under vacuum the solution of (V) in CH$_2$Cl$_2$.

$[CH_3Co(salen)NH_3]$ (XI). Obtained as orange-yellow needles by bubbling NH$_3$ into a solution of (V) in CH$_2$Cl$_2$ after addition of ether and light petroleum; air-dried at room temperature.

The ethyl, propyl, butyl derivatives prepared in the same manner loose slowly NH$_3$.

$[C_6H_5Co(salen)NH_3]$ (XII). Prepared by bubbling NH$_3$ into a solution of (VIII) in N,N-dimethylformamide, as orange-yellow needles; washed with ether and air-dried at room temperature.

$[CH_3Co(salen)C_7H_6N_2]$ $(XIII)$. A saturated methanolic solution of benzimidazole (C$_7$H$_6$N$_2$) was added to a solution of (V) in methanol. After standing a yellow solid crystallized which was washed with ethanol and dried under vacuum.

$[CH_3Co(salen)Py]$ (XIV), $[C_2H_5Co(salen)C_5H_5N]$ (XV), $[C_3H_7Co(salen)-C_5H_5N]$ (XVI) and $[C_4H_9Co(salen)C_5H_5N]$ $(XVII)$ Obtained by dissolving the aquo derivatives in pyridine, after addition of light petroleum/ether. The orange-yellow crystals were dried under vacuum at room temperature.

$[C_6H_5Co(salen)C_5H_5N]$ $(XVIII)$. Precipitated as orange-yellow needles by cooling a solution of (VIII) in ethanol and pyridine; washed with ether and dried under vacuum.

$C_6H_5Co(salen)]$ (XIX). Obtained as a green powder by heating under vacuum (VIII), (XII) and XVIII at 200°.

$[Co(salen)(CN)_2]K$ (XX). (II) dissolved in a very small quantity of water was treated with a saturated solution of KCN. The filtered crude product was dissolved in hot water and the solution was filtered into a saturated solution of KCN, whereupon

the pure solid precipitated. It was then washed with a little water and dried at 100°. (XX) may be also obtained by illuminating a solution of (V) in water and methanol in the presence of an excess of KCN. The products obtained by the two different methods have the same IR spectrum.

Thermal decomposition

(V), (VI), (VII) and (IX) were heated for 1 h under vacuum at 200°. [Co (salen)] was identified as the sole product by IR spectra (comparison with an authentical sample) and by analysis.

Magnetic measurements

Faraday method was adopted.

Spectra

The UV and visible spectra were determined using an Unicam SP 700 spectrophotometer. We have used 1 cm silica cells and 1 cm glass cells. The solvents used were reagent grade methylene chloride, pyridine and ethanol. During all the operations care was taken to avoid photochemical decomposition.

Infrared spectra were obtained using a Perkin–Elmer mod. 13C infrared spectrophotometer from nujol dispersion or KBr pellets.

SUMMARY

The preparations of stable organocobalt chelates of bis(salicylaldehyde) ethylenediimine, (salen), RCo(salen)L and RCo(salen)(R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5; L = H_2O, NH_3, pyridine, benzimidazole) are described.

The UV and visible absorption spectra are reported and briefly discussed. Evidence for the photolability of the complexes is presented.

Chemical and physico-chemical behaviour of the complexes confirm the stabilization of the cobalt–carbon bond by formation of conjugate chelate rings.

REFERENCES

1 G. COSTA, G. MESTRONI, G. TAUZHER AND L. STEFANI, J. Organometal. Chem., 6 (1966) 181.
2 G. N. SCHRAUZER AND J. KOHNLE, Chem. Ber., 97 (1964) 3056.
3 G. N. SCHRAUZER, R. WINDGASSEN AND J. KOHNLE, Chem. Ber., 98 (1965) 3324.
4 G. N. SCHRAUZER AND R. J. WINDGASSEN, Chem. Ber., 99 (1966) 602.
5 P. PFEIFFER, E. BREITH, E. LUEBBE AND T. TSUMAKI, Ann. Chem., 503 (1933) 84.
6 H. M. FAIGENBANN, L. H. VOGT, JR., AND S. E. WIBERLEY, Chem. Rev., 63 (1963) 269.
7 P. C. HEWLETT AND L. F. LARKWORTHY, J. Chem. Soc., (1965) 882.
8 S. YAMADA, H. NISHIKAWA AND E. YOSHIDA, Proc. Japan Acad., 40 (1964) 211; Chem. Abstr., 61 (1964) 7920.

9 A. E. MARTELL AND M. CALVIN, *Chemistry of the Metal Chelate Compounds*, Prentice Hall, Englewood Cliffs, N.J., 4th ed., 1959, p. 266.
10 A. EARNSHAW, P. C. HEWLETT AND L. F. LARKWORTHY, *J. Chem. Soc.*, (1965) 4718.
11 D. HALL AND F. H. MOORE, *Proc. Chem. Soc.*, (1960) 256.
12 D. HALL AND T. N. WATERS, *J. Chem. Soc.*, (1960) 2644.
13 K. PACHLER AND M. V. STACKELBERG, *Z. Anorg. Allgem. Chem.*, 305 (1960) 286.
14 J. A. HILL, J. M. PRATT AND R. J. P. WILLIAMS, *J. Chem. Soc.*, (1964) 5149.
15 Unpublished results.
16 G. C. HAYWARD, H. A. O. HILL, J. M. PRATT, N. J. VANSTON AND R. J. P. WILLIAMS, *J. Chem. Soc.*, (1965) 6485.
17 J. M. PRATT AND R. G. THORP, *J. Chem. Soc.*, (1966) 187.
18 D. DOLPHIN, A. W. JOHNSON AND R. RODRIGO, *J. Chem. Soc.*, (1964) 3186.
19 J. M. PRATT, *J. Chem. Soc.*, (1964) 5154.
20 C. J. BALLHAUSEN AND W. MOFFITT, *J. Inorg. Nucl. Chem.*, 3 (1956) 178.
21 See *e.g.* among recent contributions:
    (a) R. A. D. WENTWORTH AND T. S. PIPER, *Inorg. Chem.*, 4 (1965) 202, 709.
    (b) J. I. LEGG AND D. W. COOKE, *Inorg. Chem.*, 4 (1965) 1576; 5 (1966) 594.
    (c) K. KURODA AND P. S. GENTILE, *J. Inorg. Nucl. Chem.*, 27 (1965) 155.
22 J. H. DUNLOP AND R. D. GILLARD, *Mol. Phys.*, 7 (1963–64) 493.