Cobalt(III) Compounds of Carbanions and Their Reactivity. Part I. The Preparations and Structure of Some Malononitrilato-compounds

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Malononitrile(mnH) reacts with a variety of cobalt(III) compounds of planar quadridentate dianion Schiff-base ligands to produce cobalt alkyls of the type [Co(quadridentate)(mn)(L)] (where L is a neutral unidentate ligand). A range of solid compounds has been isolated and six-co-ordinate structures are assigned to most of them on the basis of the electronic spectra, although several may be five-co-ordinate. ^1H N.m.r. data are recorded for solutions in C_5D_5N and $(CD_3)_2SO$. The formation reaction appears to involve carbanion nucleophilic substitution at a cobalt(III) centre. The compounds undergo further reaction in pyridine to produce cyano-species of the type [Co(quadridentate)(CN)(py)].

MANY cobalt(III) alkyls of the vitamin B_{12} structural type are now known.[1-7] They are usually prepared either by the reaction of alkyl halides, *etc.*, with a reduced ' cobalt(I) ' compound,[3-6] or from cobalt(III) halogeno-species and a Grignard reagent.[1,2] Reactions of alkyl or aralkyl halides (RX) with cobalt(II) species also give cobalt alkyls, but with an equal quantity of halogeno-cobalt(III) species.[7,8] The reaction appears to occur, generally, by initial formation of a halogeno-cobalt(III) species and an alkyl radical, followed by reaction of the latter with cobalt(II) to give the ' cobalt(III)-alkyl.' [8]

As an alternative method of preparing species with a cobalt–carbon bond, we have been looking at the possibility of carbanion substitution at a cobalt(III) centre, and here report details of the preparation and properties of cobalt(III) compounds of the malononitrilato anion $\{CH(CN)_2^-$, herein abbreviated as mn}. These apparently are formed according to the generalised equation (1).

$$Co^{III}(L)_nOR + CH_2(CN)_2 \longrightarrow [Co^{III}(L)_n\{CH(CN)_2\}] + ROH \quad (1)$$

A preliminary account has been given.[9]

EXPERIMENTAL

The anions of the various ligands are abbreviated as follows:

salen = 1,2-bis(salicylideneiminato)ethane
salpn = 1,2-bis(salicylideneiminato)propane
salbn = 1,2-bis(salicylideneiminato)-2-methylpropane
saloph = 1,2-bis(salicylideneiminato)phenylene
3-OMe-salen = 1,2-bis(3-methoxysalicylideneiminato)-ethane
7-Me-salen = 1,2-bis(7-methylsalicylideneiminato)ethane
abpn = 1,2-bis(*o*-iminobenzylideneiminato)propane
dmg = dimethylglyoximate

Hydration numbers are given as integers or halves, although in some cases there may be only partial occupancy of the hydration sites. All solid species listed as hydrates had broad strong OH stretching frequencies in their i.r. spectra.

All solids were characterised by their *X*-ray powder diffraction patterns; the experimental results are deposited as Supplementary Publication, No. SUP. 20586 (4 pp.).†

Preparation of Compounds.—The compounds [Co(salen)-(OMe)] and [Co(salen)(OH)(H_2O)] have been described by Costa and his co-workers,[5,10] but they are not well-characterised species and are probably mixtures. The products we have obtained are largely non-crystalline (*X*-ray powder diffraction) and the ^1H n.m.r. spectra show the presence of paramagnetic species. Further, solutions of ' Co(salen)(OMe) ' in MeOH deposit [Co_2(salen)$_2$] [11] when set aside. Such products are, however, a convenient source of ' oxidised Co(salen) ' species, and we do not doubt that they are *largely* cobalt(III) species.

A product which is probably [Co(salen)(OH)(py)] is made by dissolving [Co(salen)(OH)(H_2O)] in pyridine followed by precipitation with ether. An oil is usually formed, but it soon hardens to a largely non-crystalline red-brown solid. It is quite soluble in chloroform and methanol.

Oxidised Co(salpn) species of the same type, with much the same properties also were prepared in the same way.

All preparations of the following malononitrilato-compounds were carried out in open vessels, with free access of atmospheric oxygen.

Compounds α-{Co(salen)(mn)}, β-{Co(salen)(mn)}, *and* [Co(salen)(mn)(H_2O)]. These compounds were the various products of the reactions of malononitrile with oxidised Co(salen) species in methanol or ethanol. The products, which were identified by *X*-ray powder photography were often mixtures, but we find the following methods to give largely the one form. (*a*) [{Co(salen)}$_2O_2$] (2·0 g) was suspended in ethanol (50 ml) and malononitrile (1·0 g) in ethanol (5 ml) was added to it. The mixture was stirred (1 h), when olive-green α-{Co(salen)(mn)} was formed (85% yield).

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. supplied as full size copies).

[1] F. Wagner and K. Bernhauer, *Ann. New York Acad. Sci.*, 1962, **112**, 580.

[2] D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc.* (*C*), 1968, 881; and references therein.

[3] G. N. Schrauzer, *Accounts Chem. Res.*, 1968, **1**, 97.

[4] F. Calderazzo and C. Floriani, *Chem. Comm.*, 1967, 139.

[5] A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta Rev.*, 1970, **4**, 41, and references therein.

[6] G. Costa, G. Mestroni, and G. Tauzher, *J.C.S. Dalton*, 1972, 450.

[7] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1966, **88**, 3738.

[8] P. W. Schneider, P. F. Phelan, and J. Halpern, *J. Amer. Chem. Soc.*, 1969, **91**, 77.

[9] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 591.

[10] G. Costa, G. Mestroni, and G. Pellizer, *J. Organometallic Chem.*, 1968, **15**, 187.

[11] S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671.

(*b*) ' Inactive ' $[Co_2(salen)_2]$ (5·0 g) was suspended in ethanol (100 ml) and malononitrile (2·0 g) was added to it. The mixture was refluxed for 3 h, and then set aside overnight. The resulting brown-green powder of β-{Co(salen)(mn)} was filtered off, washed with ethanol, and dried in the air (yields were 80—90%).

(*c*) For $[Co(salen)(mn)(H_2O)]$, [Co(salen)] (4·0 g) was dissolved in methanol (500 ml) and air was drawn through the solution (2—3 h). The resulting solution, probably containing largely [Co(salen)(OMe)(MeOH)],[10] was filtered, and malononitrile (2·0 g) in methanol (25 ml) was added to it. The brown colour soon changed to green, and green crystals of $[Co(salen)(mn)(H_2O)]$ separated out when water was added to the filtrate.

This compound also was obtained when β-{Co(salen)(mn)}, but not the α-form, was suspended in 50% aqueous acetone.

If the reaction solutions were subjected to prolonged heating, dark brown amorphous products were obtained. These have not been characterised.

[Co(salen)(mn)(py)]. Dissolution of the above malononitrilato-compounds in pyridine and addition of water gave brown crystals in yields of up to 90%.

[Co(salen)(CN)(py)]. Heating on a steam-bath of the greenish-brown pyridine solutions of the above malononitrilato-compounds for some hours gave a colour change to red-brown, and red-brown crystals of the cyano-compound separated out. The reaction occurs in the absence of light and water.

The above compound was also prepared directly by dissolving [Co(salen)] (2·0 g) in pyridine (20 ml) in the air and adding NaCN (0·5 g) in water (20 ml). The solution was filtered after 30 min, and water was added to precipitate the red-brown compound.

The two different products had identical *X*-ray powder diffraction patterns.

Compounds α-{Co(salpn)(mn)}, β-{Co(salpn)(mn)}, $[Co(salpn)(mn)(H_2O)]$, and [Co(salpn)(mn)(EtOH)]. As for the salen species, various crystalline species were obtained from the different reactions in methanol or ethanol, often as mixtures. The following methods gave products that were not detectably contaminated with other species.

(*a*) A mixture of ' active ' [Co(salpn)] (2·0 g) and malononitrile (0·5 g) in ethanol (50 ml) was heated on the steam-bath (3 h), and then set aside overnight. Green-brown crystals of the β-form were obtained (75% yield).

(*c*) A mixture of ' active ' [Co(salpn)] (2·0 g) and malononitrile (1·0 g) in ethanol (50 ml) was stirred for 1 h. Green crystals of $[Co(salpn)(mn)(H_2O)]$ formed (80% yield).

(*d*) $[(Co(salpn)(mn)(H_2O)]$ could also be obtained in yields of up to 90% by adding mnH to either an ethanol or a methanol solution of $[Co(salpn)(OH)(H_2O)]$. The solutions soon turned green, and the compound was precipitated by the addition of water.

Dehydration of $[Co(salpn)(mn)(H_2O)]$ at 110 °C *in vacuo* gave α-{Co(salpn)(mn)}.

(*e*) [Co(salpn)(mn)(EtOH] slowly replaced the aquo-species if a suspension of the latter in ethanol was set aside for several days. The presence of ethanol in the product was confirmed by its ^1H n.m.r. spectrum.

Unlike the β-salen compound, neither the α- nor the β-form of {Co(salpn)(mn)} changed when suspended in aqueous acetone.

[Co(salpn)(mn)(py)] was prepared by the method used for the analogous salen compound.

$\{Co(salbn)(mn)\},CHCl_3$. The compound [Co(salbn)][12] (1·5 g) was suspended in chloroform (10 ml) and malononitrile (0·3 g) was added to it. The olive-green solid, which had formed during 4 h of stirring, was filtered off, washed with $CHCl_3$, and dried in the air (60% yield).

[Co(salbn)(mn)(py)]. The above malononitrilato-compound (0·1 g) was dissolved in pyridine (7 ml) with some warming on a steam-bath. The solution was filtered and set aside to cool and gave *olive-green* crystals of the compound when water was added.

[Co(saloph)(mn)(MeOH)]. The compound $[Co(saloph)(OH)(H_2O)]$[5] (0·55 g) in methanol (10 ml) was treated with malononitrile (0·1 g) and the solution was stirred in the air (30 min). The dark-brown crystals, which had formed, were filtered off, washed with methanol, and dried in the air.

$[Co(3\text{-}OMe\text{-}salen)(mn),1{\cdot}5H_2O$. The compound [Co(3-OMe-salen)][13] (5·0 g) and malononitrile (1·0 g) were triturated under methanol (20 ml) in the air, and the suspension was then set aside (30 min). The green crystals, which had formed, were filtered off, washed with methanol, and dried in the air (90% yield).

$[Co(3\text{-}OMe\text{-}salen)(mn)(DMF)],0{\cdot}5H_2O$. This compound was obtained when the above product was recrystallised from *NN*-dimethylformamide.

$[Co(3\text{-}OMe\text{-}salen)(mn)(py)]2H_2O$. The preparation of this compound was the same as that used for [Co(salbn)(mn)(py)]; it gave a light brown powder (50% yield).

$[Co(3\text{-}OMe\text{-}salen)(mn)(3,5\text{-}lutidine)],2H_2O$. The preparation of this compound was the same as that used for [Co(salbn)(mn)(py)]; it gave brown crystals (50% yield).

If the solution had been heated for several hours on a steam-bath, the product was mixed with a new species, which was probably the cyano-compound (*cf.* the following pyridine species).

[Co(3-OMe-salen)(CN)(py)]. A saturated solution of the malononitrilato-compound in pyridine was heated on a steam-bath (3 h). Brown crystals separated when the solution was set aside to cool. They were filtered off, washed with water and methanol, and dried in the air.

{Co(7-Me-salen)(mn)}. The compound [Co(7-Me-salen)][5] (2·0 g) was suspended in aqueous methanol (1 : 9; 100 ml) and air was drawn through the mixture until the solid had dissolved. The brown solution was filtered and evaporated to dryness. The residue in methanol (50 ml) was treated with malononitrile (1·0 g), when the solution turned green, and slowly deposited green crystals of the compound.

[Co(7-Me-salen)(mn)(py)]. The preparation of this compound was the same as that used for [Co(salen)(mn)(py)]. Brown needles were obtained in 60% yield.

[Co(7-Me-salen)(CN)(py)]. If a pyridine solution of the malononitrilato-compound was heated on a steam-bath (3 h) and set aside to cool, brown crystals of the cyano-compound separated out. The same compound (*X*-ray powder patterns) was obtained through aerial oxidation overnight of a stirred mixture of [Co(7-Me-salen)] (2·0 g), NaCN (0·25 g), and pyridine (1 ml) in methanol (30 ml). The red-brown product was recrystallised from methanol.

$[Co(dmg)_2(mn)]$. The compound $[Co(dmg)_2]$ (1·5 g) in methanol (20 ml) was oxidised to a brown solution by drawing air through the suspension. Malononitrile (0·4 g) was added to the solution which was then set aside in the dark (48 h); brown crystals of the compound formed (30% yield).

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[12] B. M. Higson and E. D. McKenzie, in preparation.

[13] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

[Co(abpn)(mn)]. The compound [Co(abpn)][14] (2·0 g) in CH_2Cl_2 (20 ml) was treated with malononitrile (1·0 g) in CH_2Cl_2 (8 ml). The mixture was filtered and set aside. The solution gradually changed from bright red to brown, and, with slow evaporation of the solvent, eventually deposited a green-brown solid.

[Co(salen){CH(CN)CONH$_2$}(H$_2$O)]. The compound [Co(salen)(OH)(H$_2$O)] (1·0 g) in methanol (20 ml) was treated with an excess of cyanoacetamide, and the mixture was set aside overnight. The green crystals, which had formed, were filtered off and washed with methanol.

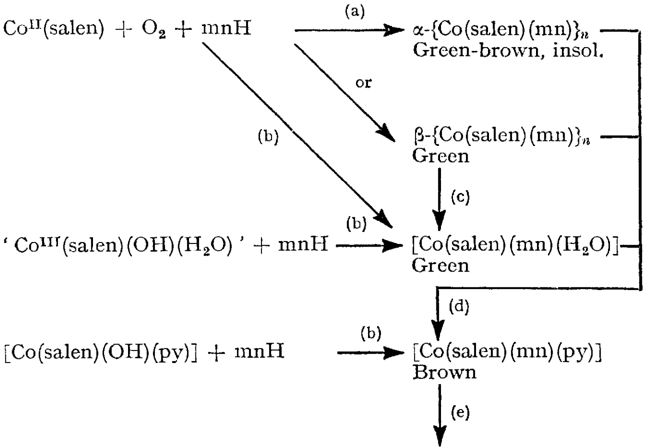
When the brown solution in pyridine was heated, crystals of [Co(salen)(py)(CN)] separated out.

[Co(salen){CH(CN)CO$_2$Et}(H$_2$O)]. A green solution formed when [Co(salen)(OH)(H$_2$O)] (0·5 g) in methanol (25 ml) was treated with an excess of ethyl cyanoacetic ester. The green compound was precipitated by adding water. This compound also gave [Co(salen)(py)(CN)] when heated in pyridine solution.

Physical Measurements.—The following instruments were used: i.r. spectra—Perkin-Elmer PE457; electronic spectra—Unicam SP 700 + SP 735; n.m.r. spectra—Varian HA100; *X*-ray powder diffraction patterns—Phillips 11·46 cm camera, with Co-K_α radiation.

RESULTS AND DISCUSSION

The crystalline solids isolated are listed in Table 1, together with the analytical data, the peak positions in the electronic spectra (visible and near i.r. regions), and the C≡N stretching frequencies in the i.r. spectra. The latter were particularly useful as a monitor of the presence of nitrile in the isolated solids. A feature of the salen and salpn systems is the variety of products obtainable from the preparations in ethanol or methanol (Schemes 1 and 2).

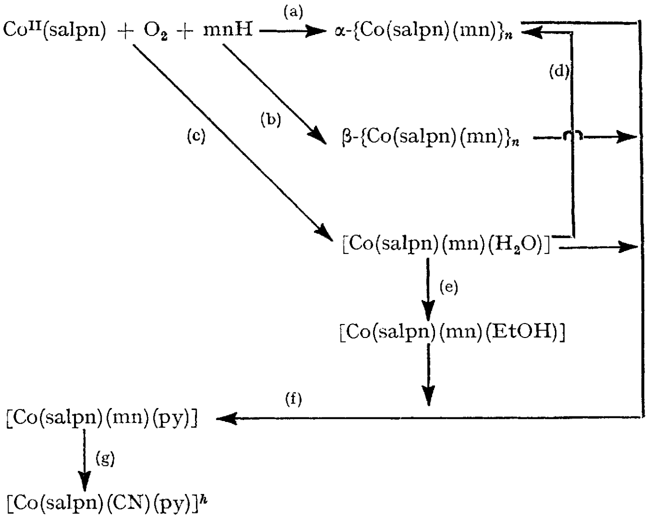


(a) In ethanol (products were apparently randomly α or β). (b) In methanol. (c) Suspended in 50% aqueous acetone. (d) Dissolved in pyridine and precipitated with water. (e) Heated in pyridine.

SCHEME 1 The salen compounds prepared

Structure of the Products.—The basic proof that these compounds contain a cobalt–carbon bond is given by a full three-dimensional *X*-ray crystal structure[9] of [Co(salpn)(mn)(py)].

We currently believe that most of the compounds are six-co-ordinate. Thus the solids which contain water, or other potential donor molecules, are assumed to be of type (I); and the non-solvated species, such as α- and β-Co(salen)(mn) are assumed to be polymers as in (II), or dimers as in (III). There is some doubt about the nature of α-Co(salpn)(mn). The analytical data consistently (four independent samples) gave high nitrogen figures, indicating perhaps the presence of an excess of malononitrile. They certainly point to an anhydrous species, but the i.r. spectra gave the following bands in the OH (NH?) region: 3440ms, 3345s, 3235ms, and 3190ms cm^{-1}. It could, however, be converted in good yield into the pyridine compound [Co(salpn)(mn)(py)].



(a) In methanol—heated and set aside. (b) In ethanol—heated and set aside. (c) In ethanol at ambient temperature. (d) Dehydrated at 100 °C. (e) Suspended in ethanol for several days. (f) Dissolved in pyridine and precipitated with water. (g) Heated in pyridine solution. (h) Not isolated from solution.

SCHEME 2 The salpn compounds prepared

Six-co-ordinate structures are consistent with, but not proven by, the electronic spectra (Table 1). Costa and his co-workers[15] recently seem to imply that the co-ordination number of such cobalt alkyls can be determined from the electronic spectra, with five-co-ordinate compounds having bands in the region 16—13 kK, and six-co-ordinate ones in the region above 18 kK. However, this is certainly not true. For the present compounds, we note that [Co(salpn)(mn)(py)] is known[9] to be six-co-ordinate, and has its band at 16·6 kK; that most of the other compounds have very similar spectra; and that the band positions vary in the manner expected from the position in the spectrochemical series of the (assumed) axial ligands. Possible five-co-ordinate compounds in the present series are [Co(abpn)(mn)] and [Co(dmg)$_2$(mn)], which have bands at quite low energy (Table 1).

The ^{1}H n.m.r. spectra (Table 2) of the quadridentate

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[14] B. M. Higson and E. D. McKenzie, *J.C.S. Dalton*, 1972, 269.

[15] G. Tauzher, G. Mestroni, A. Puxeddu, R. Costanzo, and G. Costa, *J. Chem. Soc.* (*A*), 1971, 2504.

TABLE 1

The compounds prepared, the analytical data, the C≡N stretching frequencies from the i.r. spectra, and the electronic spectra in the region 5—25 kK.

Compound	Analyses (%) Found C	H	N	Analyses (%) Calculated C	H	N	I.r. spectra (cm^{-1})	Electronic spectra (kK) [a]
α-{Co(salen)(mn)}$_n$	58·1	4·4	14·7	58·5	3·9	14·4	2223s	(21) 14·5 (9·4)
β-{Co(salen)(mn)}$_n$	57·7	4·2	15·0	58·5	3·9	14·4	2260s, 2222m	(15)
[Co(salen)(mn)(H_2O)]	55·6	4·2	13·6	55·9	4·2	13·7	2235s, 2225s	(21) 14·6 (9·8)
[Co(salen)(mn)(py)]	61·5	4·0	14·7	61·4	4·3	14·9	2222s	
[Co(salen)(CN)(py)]	61·0	4·5	13·2	61·4	4·5	13·0	2140m, 2125m	(20·8)
α-{Co(salpn)(mn)}$_n$	58·3	4·2	14·1	59·4	4·2	13·9	2218s	(21) (16)
β-{Co(salpn)(mn)}$_n$	58·7	4·4	14·0	59·4	4·2	13·9	2230ms, 2216s	(21) 14·1 (9)
[Co(salpn)(mn)(H_2O)]	57·2	4·9	13·1	56·9	4·5	13·3	2222s	(21) 15·0 (10·5)
[Co(salpn)(mn)(EtOH)]	58·7	5·1	12·8	58·7	5·2	12·4	2221s	(21·6) 15·3
[Co(salpn)(mn)(py)]	62·3	4·9	14·7	62·1	4·6	14·5	2223ms, 2220s	(20·2) 16·6 (10·8)
{Co(salbn)(mn)}$_n$$CHCl_3$	49·9	4·3	11·4 [b]	49·1	3·8	10·4	2221s	(20·9) 15·1 (10·2)
[Co(salbn)(mn)(py)]	62·3	5·0	14·0	62·8	4·9	14·1	2228s, 2216s	(19·7) 16·4 (10·1)
[Co(saloph)(mn)(MeOH)]	60·7	4·7	11·9	61·3	4·1	11·9	2224m	
[Co(3-OMe-salen)(mn)(H_2O)],0·5H_2O	52·9	4·9	11·0	52·8	4·6	11·7	2220s	(20·8) 15·5 7·3
[Co(3-OMe-salen)(mn)(DMF)]H_2O	54·2	5·6	12·9	53·3	5·2	12·9	2222s, 2130w	(20·7) 15·4 (10)
[Co(3-OMe-salen)(mn)(py)]2H_2O	55·0	5·1	12·1	55·2	5·0	12·4	2220s	(20·4) (15·9) (10·1)
[Co(3-OMe-salen)(mn)(3,5-lutidine)]2H_2O	55·4	5·7	11·6	56·6	5·4	11·8	2221s	(20·8) (16·1) (10·5)
[Co(3-OMe-salen)(CN)(py)]	59·2	5·0	11·6	58·8	4·7	11·4	2140m	
{Co(7-Me-salen)(mn)}$_n$	59·7	4·8	13·1	60·0	5·0	13·3	2228s	(20·4) 15·0 (10·2)
[Co(7-Me-salen)(mn)(py)]	62·0	5·1	13·6	62·8	4·9	14·1	(2220)ms, 2218s	(19·5) (16·2) (11·3)
[Co(7-Me-salen)(CN)(py)]	62·7	5·2	12·1	62·6	5·5	12·2	2140s	(18·9) (12·5)
[Co(dmg)$_2$(mn)]	37·8	5·3	22·1	37·3	4·3	23·7	2222s	20·6 (18·6) 11·5
[Co(abpn)(mn)]	59·3	4·9	21·1	59·7	4·8	20·9	2215s	(20·7) 13·4 8·45
[Co(salen){CH(CN)COOEt}(H_2O)]	55·4	5·1	9·1	55·4	4·9	9·2	2210s	15·2 (10·2)
[Co(salen){CH(CN)CONH$_2$}(H_2O)]	53·7	4·3	13·1	53·5	4·5	13·1	2220s	(16·3) (10·7)

[a] These are the band positions from the diffuse reflectance spectra. Bands appearing as shoulders are given in parentheses.
[b] Cl analyses: Found, 16·0; Calc., 19·8%.

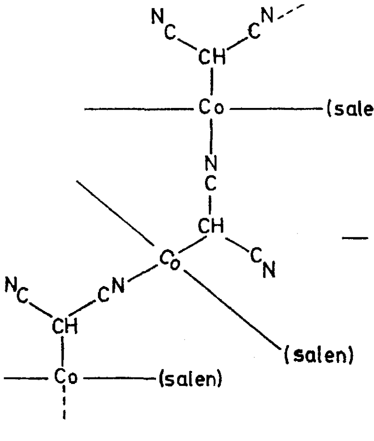
TABLE 2

The ^1H n.m.r. data (τ values) [a]

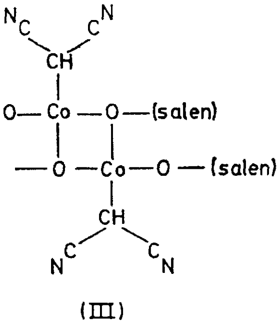
Compound [b]	Solvent	Quadridentate Schiff base ligand CH=N	Aromatic CH [c]	Aliphatic CH	CH of mn	Other resonances
{Co(salen)(mn)}	C_5D_5N [d]	1·79 (s)	2·5—2·9 (m) 3·58 (t)	5·90 (s) [C_2H_4]	5·48 (s)	
[Co(salpn)(mn)(H_2O)]	$(CD_3)_2SO$	1·83 (s, 1) 1·91 (s, 0·6) 1·95 (s, 0·4)	2·6—3·0 (m, 6) 3·4—3·65 (m, 2)	5·75—6·8 (m, 3) [CH_2–CH] 8·33 (d, 1·2) 8·48 (d, 1·8) [Me]	6·30 (s, 0·6) 6·36 (s, 0·4)	
[Co(salpn)(mn))py)]	$CDCl_3$	1·99 (s, 0·5) 2·06 (s, 1) 2·14 (s, 0·5)	2·6—3·0 (m) 3·3—3·6 (m, 2)	5·6—6·25 (m, 2) 6·4—6·8 (m, 1) [CH_2–CH] 8·30 (d, 1·2) 8·58 (d, 1·8) [Me]	5·96 (s, 0·4) 6·03 (s, 0·6)	1·75 (d, 2), 2·36 (t, 1) 2·6—3·0 (m) [py]
	C_5D_5N	1·70 (s, 1) 1·77 (s, 0·5) 1·84 (s, 0·5)	2·5—3·0 (m, 6) 3·4—3·7 (m, 2)	5·6—6·6 (m, 3) [CH_2–CH] 8·32 (d, 1·5) 8·60 (d, 1·5) [Me]	5·38 (s, 0·5) 5·52 (s, 0·5)	
{Co(salbn)(mn)}$CHCl_3$	$(CD_3)_2SO$	1·82 (s, 1) 1·87 (s, 1)	2·6—3·1 (m, 6) 3·4—3·7 (m, 2)	5·97, 6·11, 6·22, 6·36 (AB2)[CH_2] 8·23 (s, 3) 8·55 (s, 3) [Me]	6·17 (s, 1)	
	C_5D_5N [d]	1·68 (s, 1) [e]	2·5—2·95 (m) 3·43 (t)	5·95, 6·11, 6·37, 6·51 (AB)[CH_2] 8·02 (s) 8·30 (s) [Me]	5·51 (s)	
[Co(3-OMe-salen)(mn)(H_2O)]	C_5D_5N	1·78 (s, 2) 1·60 (s, 0·25) [f]	3·16 (d, 2, J = 7) 3·32 (d, 2, J = 7·5) 3·63 (t, 2, J = 7)	5·77 (br AB4) [C_2H_4]	5·13 (s, 1)	6·26 (s, 6) [OMe] 6·45 (s, 0·75) [f]
[Co(3-OMe-salen)(mn)(DMF)]	C_5D_5N	1·82 (s, 2)	3·15—3·40 (m, 4) [g] 3·66 (t, 2, J = 8)	5·80 (s, 4) [C_2H_4]	5·16 (s, 1)	6·28 (s, 6) [OMe] 6·40 (s, 0·75) [f] 2·00 (s, 1) 7·32 (s, 3) 7·38 (s, 3) [DMF]
	$(CD_3)_2SO$	1·80 (s, 2)	3·0—3·3 (m, 4) [g] 3·58 (t, 2, J = 8)	6·02 (br, AB4) [C_2H_4]	[h]	6·14 (s, 6) 2·05 (s, 1) 7·11 (s, 3) 7·26 (s, 3) [DMF]
{Co(7-Me-salen)(mn)}$_n$	$(CD_3)_2SO$		2·38 (1), 2·46 (1), 2·84 (2), 2·88 (2) 3·4—3·6 (m, 2)	5·85, 5·95, 6·00, 6·13 [AB4)[C_2H_4]	[h]	7·30 (s, 6) [Me]
	C_5D_5N		2·5—3·0 (m, 6) 3·4—3·8 (m, 2)	5·81 (s, 4) [C_2H_4]	5·65 (s, 1)	7·37 (s, 6) [Me]
Co(saloph)(mn)(MeOH)]	$(CD_3)_2SO$	1·16 (s, 2)	2·3—3·0 (m) 3·3—3·6 (m, 2) 1·6—1·95 (m, 2) 2·3—3·0 (m) [C_6H_4]		6·32 (s, 1)	5·59—6·2 (m) 6·78 (t) [MeOH]

[a] The multiplicities given in parentheses are the gross ones. In many cases, the components had a fine structure resulting from long-range coupling. The figure also given in parentheses is the relative intensity. [b] This column gives the compound used for preparing the solution. We assume that in C_5D_5N and $(CD_3)_2SO$ the solvent is also the sixth ligand. [c] Here we can usually separate the complex resonances of the 3H, 4H, and 6H of the salicyl moiety from the 5H signals, which are further upfield. The latter is sometimes a well-defined triplet. Where other aromatic protons give signals in this region, we do not quote relative intensities. [d] Because of low solubility, a reliable measure of relative intensities was not obtained; but qualitatively they were as expected. [e] The second signal here is probably lost under the adjacent $CHCl_3$ resonance. [f] These resonances indicate the presence of a small amount of another species in the solution. [g] This multiplet has the appearance of two overlapping doublets. [h] This resonance is probably lost under the HDO resonance at τ 6·6.

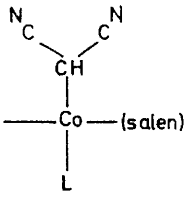
ligands are unexceptionable. As expected, either for a five-co-ordinate or a six-co-ordinate structure (I) with different axial ligands, the aliphatic chelate ring protons



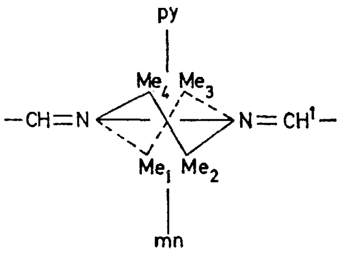
(II)



(III)



(I)



(IV)

give the fine structure which indicates that interconversion of the conformers of this chelate ring is slow on the n.m.r. time scale.

The resonances of the malononitrilato-proton in the various compounds are in the range 5—7 τ, and the position varies with the axial ligand (py or Me_2SO) and the quadridentate ligand. However, there is a large difference between the position of the resonance for [Co(salpn)(mn)(py)] in $CDCl_3$ and C_5D_5N. Thus unknown solvent effects render meaningless any interpretation of these resonances in terms of *cis*- and *trans*-effects. These protons exchange readily with D_2O.

The two malononitrilato-signals observed for the salpn compounds were investigated as a possible indication that five- and six-co-ordinate species were present in equilibrium in the solutions. They result, however, from isomerism in the six-co-ordinate species. Relative intensities did not vary with pyridine concentration, nor, in other than a random manner, over the temperature range 0—70 °C in C_5D_5N. They can be explained, together with the three azomethine proton signals (relative intensities 2 : 1 : 1), and the two methyl doublets by reference to diagram (IV).

Here we represent the four possible *equatorial* methyl positions arising from the two possible 'gauche' conformations of the 1,2-diaminopropane chelate ring. This leads to two sets of two equivalent methyl and malononitrilato-signals. They may be of varying relative intensity, but the same ratio of intensities should occur in both—as observed. Further, because the axial ligands (py and mn) are different, four azomethine proton types are generated, although two of these (the two pairs of azomethines remote from the methyls) may not differ significantly. This leads to three signals in the ratio (1 + 1) : 1 : 1—as observed.

In the case of the 3-OMe-salen compounds in pyridine, low intensity satellites of the methyl proton resonances may represent a small amount of a five-co-ordinate species.

The Formation Reaction.—Although the reactions were initially designed as carbanion substitutions, the mechanism remains in doubt, and we are currently planning kinetic studies.

There is no doubt that the reaction involves a cobalt(III) species. In contrast to the benzyl halides,[16] mnH does not react with cobalt(II) species in the absence of oxygen. Yields varied for the cobalt(III) reactions, but in many cases were in excess of 80%.

In agreement with the carbanion hypothesis, the formation of the mn compounds is fast, whereas the formation of the analogous acetonitrilato-compound $\{Co(salen)(CH_2CN)\}_n$ is quite slow.[5,17] Colour changes associated with formation of the mn compounds occur immediately the solutions are mixed; whereas the preparation of the acetonitrilato-compound takes some days at 20 °C. This difference is in agreement with the published pK_a values and rate constants: $pK_a = 12$ and $k = 1{\cdot}5 \times 10^{-2}\ s^{-1}$ for mnH, whereas $pK_a = 25$ and $k = 6{\cdot}7 \times 10^{-10}\ s^{-1}$ for MeCN. However, unless the deprotonation rate for mnH is very much faster under our reaction conditions (base-catalysed?), the observed reactions are too fast for a mechanism involving preformation of a carbanion.

Decomposition to Cyano-compounds.—All the mn compounds, and the related compounds of cyanoacetamide and the ethyl ester, decompose when heated in pyridine to the cyano-species [Co(quadridentate)(CN)(py)]. The analogous benzylnitrilato-compounds also undergo this reaction (more readily than the mn compounds) but $[Co(salen)(CH_2CN)]$ does not.[17] The latter can be recovered in very good yield as $[Co(salen)(CH_2CN)(py)]$ after several days of refluxing in pyridine.[17]

Proof of the structure of the cyano-products was obtained by preparing them directly from, for example, [Co(salen)], and NaCN in pyridine.

Here again the i.r. spectra are a useful monitor of reaction. Whereas the nitrilato-compounds all have C≡N stretching frequencies significantly above 2200 cm^{-1}, those of the cyano-species are at distinctly lower energy (Table 2). The doublet of solid [Co(salen)(CN)(py)] is particularly characteristic.

Discussion of the mechanism of this reaction and possible parallels awaits evidence of the fate of the

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[16] L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, 1971, **93**, 1374, and references therein.

[17] D. Cummins, B. M. Higson, and E. D. McKenzie, unpublished data.

CH–CN grouping. We have not yet obtained reliable g.l.c. data from the mn reactions in pyridine; but the mass spectra of the residues of the reactions of substituted phenylacetonitriles with [Co(salen)(OH)(H_2O)] in methanol in the air {which produce [Co(salen)(CN)(H_2O)]} prove the presence of the benzaldehydes. This suggests the formation of carbon radicals.

The reaction of the malononitrilato-compounds occurs in the dark in dried pyridine.

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