The Mixed Ligand Cobalt(III) Compounds of β-Diketonates and Quadridentate Dianion Schiff Bases

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A structural study is reported of the mixed chelate compounds of cobalt(III) with the quadridentate dianion ligand *NN'*-ethylenebis(salicylideneiminate) (salen and some methyl substituted analogues) and some potentially bidentate monoanion ligands: β-diketonates, salicylaldehyde, and ω-nitroacetophenone. Structures in solution have been correlated with solid state structures, now known from recent three-dimensional *X*-ray crystallographic studies. Reliance is largely on n.m.r. (^{1}H and ^{19}F) data, with some help from the i.r. and visible and u.v. electronic spectra. The compounds generally have a distorted octahedral six-co-ordinate structure with a non-planar strained salen moiety. Evidence is reported for isomers of many of the compounds and their interconversion, giving equilibrium mixtures in solution. Their range of stability has been investigated, and it is shown that in donor solvents reaction occurs giving the species [Co(salen)(solvent)$_2$][β-diketonate], in which the quadridentate ligand regains its more stable, essentially planar structure. No evidence could be found for species in which the β-diketonate is bonded to the metal in an alternative mode through the methylene carbon atom.

SINCE no evidence previously had been presented for a non-planar array of the four donor atoms of the ligands (I) in their metal compounds [where (I) = salen for R = R' = H; salpn for R = H and R' = Me; and salbn for R = R' = Me] and since a non-planar configuration must involve significant distortion of the ligand geometry, we thought the recently reported[1] cobalt(III) species [Co(salen)(β-diketonate)] to be worthy of further study. One possible alternative to the proposed structure (II), with a bidentate(*O,O*) β-diketonate, is a structure (III). That is, a cobalt(III) alkyl formed by a carbanion substitution process of the type found for malononitrile.[2] (Analogous alkyls are formed by acetone and acetonitrile under the same reaction conditions [2,3]

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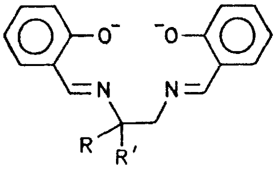
[1] S. N. Poddar and D. K. Biswas, *J. Inorg. Nuclear Chem.*, 1969, **31**, 565.

[2] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 591; D. Cummins, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, 1973, 414.

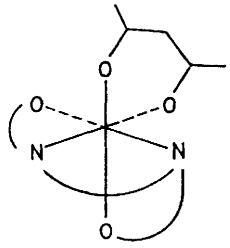
[3] A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta Rev.*, 1970, **4**, 41.

as are compounds with a whole range of compounds containing the $-CH_2CN$ group.[2])

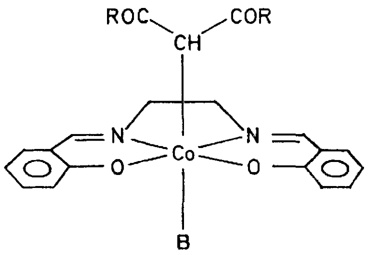
However, in none of an extended series of these compounds, here reported, can we find evidence for an alkyl species (III). The green compounds of the class first described by Poddar and Biswas [1] (and since by Costa and co-workers [3] and Cozens and Murray [4]) do indeed have the proposed structure (II), with a strained non-planar quadridentate ligand. This is proven in the solid state for two compounds by *X*-ray analyses,[5,6] and we now show that it is retained in non-donor solvents. However, we further show that rearrangements occur in donor solvents, such as pyridine and dimethyl sulphoxide (DMSO), to give species with a planar salen ligand when there are electron-withdrawing substituents on the β-diketonate skeleton; but the products are of the type $[Co(salrn)(py)_2]^+[\beta\text{-diketonate}]^-$, and again we can find no evidence for a Co–C bond in these compounds.



(I)



(II)



(III)

EXPERIMENTAL

The abbreviations for the quadridentate ligands (I) are given above. We shall use the general abbreviation salrn to cover all three.

The β-diketones used are abbreviated as follows: acetylacetone or pentane-2,4-dione(acacH), benzoylacetone or 1-phenylbutane-1,3-dione(bzacH), dibenzoylmethane or 1,3-diphenylpropane-1,3-dione(dbmH), 1,1,1-trifluoroacetylacetone or 1,1,1-trifluoropentane-2,4-dione(tfacacH), hexafluoroacetylacetone or 1,1,1,5,5,5-hexafluoropentane-2,4-dione(hfacacH), 1-(2′-thienyl)-4,4,4-trifluorobutane-1,3-dione-(tftaH); and salicylaldehyde and ω-nitroacetophenone are abbreviated as salH and ω-napH, respectively.

Hydration numbers are given as integers or one half, although in some cases the analytical data (Table 1) favour only partial occupancy of the hydration sites in the crystal, as in the case [6] of $[Co(salen)(acac)],0{\cdot}7H_2O$. All solid species quoted as containing water or alcohol showed broad strong OH stretching frequencies in their i.r. spectra.

Preparation of Compounds.—The cobalt(II) compounds [Co(salen)], [Co(salpn)], and [Co(salbn)] were prepared by the method which Diehl *et al.*[7] described for the former. Both the salen and salpn compounds were obtained as red-brown solids which soon darkened in the air as they reacted with oxygen, but the salbn compound was an orange-red solid, inactive towards oxygen.

The following preparations could also use the ' inactive ' forms of Co(salen) and Co(salpn), obtained by the method of Bailes and Calvin,[8] but these often required much longer reaction times.

[Co(salen)(bzac)], $[Co(salen)(bzac)],1{\cdot}5H_2O$, *and* $[Co(salen)(bzac)],CHCl_3$. Preparation in water followed by acetone extraction,[1] gave dark green crystals of the hydrate in low yield. It was a crystal of this batch that was used in the *X*-ray analysis,[5] and we have since checked by comparing observed and calculated powder patterns that the crystal was representative of the total batch.

When covered with $CHCl_3$, these crystals were soon replaced by the anhydrous compound α-[Co(salen)(bzac)].

An alternative preparation, which is our general method, was used here. Co(salen) (2·0 g) was suspended in ethanol (60 ml) in an open beaker, and benzoylacetone (0·98 g) was added. The mixture was then heated on the steam-bath (1 h), when the now green solution was filtered from some $[Co(salen)]_2$ which had separated out. Addition of water to the filtrate gave a green precipitate of the compound.

Three such preparations were made. One gave a crystalline green compound β-[Co(salen)(bzac)]. When recrystallised from chloroform, the product was not the α-form, but $[Co(salen)(bzac)],CHCl_3$. A second preparation gave a poorly crystalline product, the *X*-ray powder pattern of which was very faint and showed only the β-form. Recrystallisation of this product from chloroform gave α-[Co(salen)(bzac)]. The product of the third preparation was dissolved in chloroform and precipitated with light petroleum, giving a roughly equal mixture of α- and β-[Co(salen)(bzac)].

Such different products may represent the two expected isomers, but all equilibrate to the same mixture in DMSO solution.

The other preparations were generally from ethanol as above. Many of the compounds crystallised from the reaction mixtures, but some required the addition of water or light petroleum (b.p. 40—60°).

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[4] R. J. Cozens and K. S. Murray, *Austral. J. Chem.*, 1972, **25**, 911.

[5] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, 1972, 503.

[6] M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1970, 1079; M. Calligaris, G. Manzini, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1972, 543.

[7] H. Diehl and C. C. Hach, *Inorg. Synth.*, 1950, **3**, 196.

[8] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1967, **69**, 1886.

[Co(salbn)(hfacac)] *and* [Co($C_{11}C_{15}N_2O$)$_2$][hfacac] (IV).—The former has not been obtained in analytically pure form. Typically, a preparation from ethanol, as in the general method, gave a green solution within a few minutes. Addition of water then gave a green precipitate of the crude compound. This was extracted with boiling n-hexane (1 l), the solution was filtered and reduced in bulk on a rotary evaporator. Green crystals of [Co(salbn)(hfacac)] separated from the solution. They gave a good ^1H n.m.r. spectrum (*q.v.*), but poor analyses.

If the original reaction mixture was heated on the steam-bath (2 days), allowing slow evaporation of the solution to *ca.* 10 ml, and this was then set aside to cool, red-brown crystals of compound (IV) separated out. Addition of water to the filtrate then gave an, initially oily, precipitate of a mixture of the two compounds.

[Co(abpn)(tfta)].—Solutions of [Co(abpn)][9] (2 g) in dichloromethane (50 ml) and tftaH (1·3 g) in dichloromethane (20 ml) were mixed in an open beaker. The initially red solution soon turned brown, and slowly deposited dark brown-green microcrystals of the compound. These were filtered off and washed with a mixture of equal volumes of dichloromethane and light petroleum.

[Co(salen)(py)$_2$][hfacac].—From a cold concentrated solution of [Co(salen)(hfacac)] in pyridine, the solvent was removed under reduced pressure. The oily residue was dried over silica gel, and then dissolved in dry chloroform. The brown solid was precipitated from this solution by the rapid addition of light petroleum (b.p. 40—60°). So precipitated, it did not detectably diffract *X*-rays, but was characterised by the analytical and ^1H n.m.r. data.

If the solution was heated at any stage, the desired product was not obtained.

[Co(salen)(py)(H_2O)]BF_4.—To solutions of [Co(salen)(py)$_2$]X (where X = hfacac or tfta) (2 g) in cold pyridine (saturated solutions) $NaBF_4$ (0·5 g) was added, followed by diethyl ether. The light brown solids which precipitated were filtered off, and then extracted with chloroform (white residue). Addition of diethyl ether to the chloroform solutions gave brown crystals of the compound.

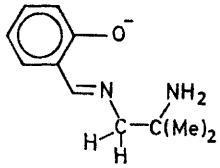
Reaction of [Co(saloph)] *with benzoylacetone.* [Co(saloph)][3] (1·5 g) and benzoylacetone (0·75 g) were heated together in ethanol (50 ml) for 4 h. The red solution was then filtered from unreacted solid and heated for a further 6 h, when dark green crystals of [Co(bzac)$_3$] were deposited. The latter was characterised by the analytical data and its mass spectrum.

Physical Measurements.—Details have been given previously.[9]

RESULTS AND DISCUSSION

The compounds isolated and studied, most of which are new, are listed in Table 1.

Of all the various preparations tried here, only one failed to give a pure sample of the mixed ligand compound. Green [Co(salbn)(hfacac)], which is formed initially in ethanol, rearranges to compound (IV), a brown bis-terdentate cationic species [Co($C_{11}H_{15}N_2O$)$_2$][hfacac] in which the terdentate ligand is shown (V).



(V)

The structure of compound (IV) is proven by the analytical and i.r. data (NH stretching frequencies) and especially by its ^1H n.m.r. spectra.

For the various green compounds, the spectroscopic, and particularly the n.m.r. data show unequivocally that structure (II) (already proven for the solid state [5,6]) is retained in solution in non-donor solvents.

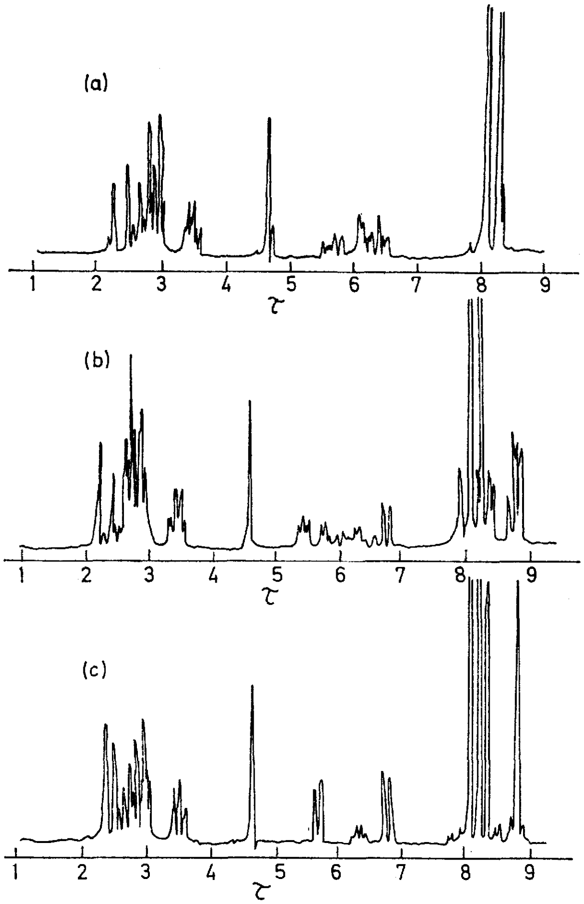


FIGURE 1 The ^1H n.m.r. spectra in $CDCl_3$ of (a) [Co(salen)(acac)], (b) [Co(salpn)(acac)], and (c) [Co(salbn)(acac)]

*N.M.R. Data.**—Assignments of the various resonances are generally unambiguous, and the general features of the ^1H n.m.r. spectra of the green compounds (representative examples of which are given in Figure 1) are: (*a*) Two low-field azomethine (CH=N) resonances generally are observed (with some complications from isomerism and rearrangement, *q.v.*). This is evidence [6] in favour of structure (II) for the salen compounds, but

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* The Supplementary Publication No. SUP 20687 (24 pp., 1 microfiche) contains: (*i*) electronic spectra 30—5 kK; (*ii*) infrared spectra 1500—1800 cm^{-1}; (*iii*) mass spectra; (*iv*) ^1H n.m.r. spectra; and (*v*) ^{19}F n.m.r. spectra. For details of the Supplementary Publications scheme see Notice to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Index Issue.

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

not for the compounds of the unsymmetrical salpn and salbn ligands. It is not, however, an invariable rule. In spite of their non-planar configuration (evidence from the other n.m.r. resonances, for example), and the fact that they are mixtures of isomers, both [Co(salpn)(tfacac)] and [Co(salpn)(tfta)] in $CDCl_3$ give only one, rather broad, resonance here, which splits into two in the presence of water or ethanol. The latter apparently form hydrogen bonds to one of the phenolic oxygens of the cobalt compound as in the crystalline compounds.[5,6]

' Solvent effects ' are also quite marked in this region. Compare, for example, the spectra of [Co(salen)(acac)] in $CDCl_3$ and $(CD_3)_2SO$; and a further complication in using just these resonances [6] to assign structure is the fact that in some cases there is an overlap with the adjacent salicyl multiplet.

(*b*) The aromatic protons of the salicyl moiety give a complex multiplet for the protons in positions **3**, **4**, and **6**; but the **5**-proton is invariably at higher field, and usually recognisable as two overlapping triplets. (This assignment is based on direct parallels with a range of diamagnetic nickel(II) and cobalt(III) salicylaldimines with various substituents on the salicyl ring.)

TABLE 1

The compounds prepared, and the analytical data. Except for those few, the different colours of which are given in a footnote, the compounds were green

		Found				Calculated			
Compound	Source	C	H	N	Others	C	H	N	Others
[Co(salen)(acac)]	*a*	59·7	5·1	6·7		59·4	5·0	6·6	
[Co(salen)(acac)]H_2O	*a*	56·9	5·1	6·6		57·0	5·3	6·3	
α-[Co(salen)(bzac)]	*a, d*	64·2	5·1	5·7		64·2	4·8	5·8	
β-[Co(salen)(bzac)]	*d*	64·6	5·3	5·7		64·2	4·8	5·8	
[Co(salen)(bzac)]1·5H_2O	*d*	61·3	5·0	5·8		60·8	5·1	5·5	
[Co(salen)(bzac)]$CHCl_3$	*d*	53·7	3·9	4·8	Cl, 17·7	53·5	4·0	4·6	Cl, 17·6
[Co(salen)(dbm)]	*e*	68·0	4·8	5·0		67·9	4·6	5·1	
[Co(salen)(hfacac)]	*e*	47·9	3·0	5·3		47·4	2·9	5·3	
[Co(salen)(tfacac)]	*e*	52·8	3·8	5·9		52·7	3·8	5·9	
[Co(salen)(tfta)]	*e*	52·3	3·5	5·3	S, 5·3	52·8	3·3	5·1	S, 5·9
[Co(salen)(sal)]	*e*	61·7	4·5	6·4		61·7	4·5	6·3	
[Co(salen)(ω-nap)]$CHCl_3$	*f*	48·9	3·8	6·9	Cl, 17·3	49·3	3·5	6·9	Cl, 17·5
[Co(salpn)(acac)]	*g*	60·2	5·1	6·4		60·3	5·3	6·4	
[Co(salpn)(acac)]2H_2O,EtOH	*e*				wt. loss, 15·4 [b]				2H_2O + 1EtOH, 15·8
[Co(salpn)(bzac)]	*e, h*	64·8	5·3	5·8		64·8	5·1	5·6	
[Co(salpn)(bzac)]H_2O	*e, h*	62·5	5·4	5·4		62·6	5·3	5·4	
[Co(salpn)(dbm)]	*e*	68·4	4·9	4·8		68·3	4·9	5·0	
[Co(salpn)(hfacac)]	*e*	48·9	3·7	5·3		48·4	3·1	5·1	
[Co(salpn)(tfacac)]	*e, i*	53·0	4·3	5·6		53·7	4·1	5·7	
[Co(salpn)(tfta)]1·5H_2O,EtOH	*c*				wt. loss, 11·8 [b]				1·5H_2O + EtOH, 11·6
[Co(salpn)(tfta)]	*e, i*	53·8	3·7	5·3	S, 6·0	53·6	3·6	5·0	S, 5·7
[Co(salpn)(sal)]	*e*	62·5	4·7	6·2		62·5	4·8	6·1	
[Co(salpn)(sal)]H_2O	*e*	61·6	5·1	5·7		60·3	4·9	6·0	
[Co(salbn)(acac)]	*e*	60·9	5·9	6·1		61·1	5·6	6·2	
[Co(salbn)(acac)H_2O	*e*	58·9	5·4	6·0		58·7	5·8	6·0	
[Co(salbn)(bzac)]	*e, j*	65·7	5·4	5·4		65·4	5·3	5·4	
[Co(salbn)(bzac)]EtOH	*c*	64·7	6·1	4·9		64·3	5·9	5·0	
[Co(salbn)(dbm)]	*e*	67·9	5·4	4·7		68·8	5·0	4·9	
[Co(salbn)(hfacac)]	*d*								
[Co(salbn)(tfacac)]	*e*	54·5	5·1	5·2		54·4	4·5	5·5	
[Co(salbn)(tfta)]EtOH	*e*	54·3	4·4	4·6	S, 5·8	54·2	4·6	4·5	S, 5·2
[Co(salbn)(sal)]	*c*	63·3	5·2	6·1		63·3	4·9	5·9	
[Co(salbn)(ω-nap)] [c]	*e, j*	59·9	5·5	7·8		60·4	4·7	8·1	
[Co(salbn)(ω-nap)]H_2O [c]	*e*	58·3	5·1	7·6		58·3	4·9	7·9	
[Co(salen)$(py)_2$][hfacac] [c]	*d*	53·3	3·7	8·0		53·9	3·7	8·1	
[Co(salen)$(py)_2$][tfta] [c]	*d*	58·9	4·2	8·2	S, 4·3	58·7	4·0	7·8	S, 5·8
[Co(salen)(H_2O)(py)]BF_4 [c]	*d*	49·4	4·2	8·4		49·5	4·2	8·3	
[Co(abpn)(tfta)] [c]	*d*	53·8	4·0	9·9	S, 5·7	53·8	5·0	10·0	S, 5·8
[Co$(C_{11}H_{15}N_2O)_2$][hfacac] [c] [Compound (IV)]	*d*	51·5	5·8	8·5		50·0	4·8	8·6	

[a] These were reported by Poddar and Biswas, ref. 1. [b] ' Wt. loss ' refers to the weight lost at equilibrium at 60 °C *in vacuo*. [c] These compounds were various shades of brown. [d] See Experimental section. [e] Preparation was by the general method from ethanol. [f] The compound was recrystallised from chloroform. [g] The compound was recrystallised from acetone. [h] The products were commonly mixtures of the anhydrous species and the hydrate (*X*-ray powder data). [i] It was generally necessary to pass this product down a short alumina column in $CHCl_3$ to remove brown paramagnetic impurities. [j] The product was recrystallised from benzene.

(*c*) The resonance of the γ-proton of the β-diketonate occurs near τ 4, as in many other chelated β-diketonates; but at significantly lower field than that of the proton of a variety of malononitrilatocobalt(III) species,[2] in which there is a Co–CH moiety.

These protons readily undergo exchange reactions with D_2O.

(*d*) The aliphatic methylene protons invariably give complex unsymmetrical multiplets, and can be interpreted as arising only from a structure in which all are non-equivalent.

The spectra of the salbn compounds are relatively simple, with an AB multiplet for the methylene protons, and two well separated signals for the non-equivalent methyls.

The spectra of the salpn compounds are markedly complicated by isomerism (*q.v.*). Two methyl doublets of different relative intensity are generally observed, and the resonances of the CH_2–CH protons are complex. Some of the resonances of the most abundant isomer can be distinguished, and are of the type expected for a rigid structure (II). However, we have not attempted to analyse completely a system which may result in some cases from as many as six isomers.

(*e*) The resonances of the various β-diketonate substituents also give important evidence for structure (II) in solution. The acetylacetonate compounds all give two distinct methyl resonances; and the ^{19}F spectra of the green hfacac compounds in non-donor solvents also show non-equivalence of the CF_3 groups. Although the spectrum of [Co(salbn)(hfacac)] in $CDCl_3$ is a broad singlet down to -60 °C, two well resolved signals are obtained in CCl_4 solution. There are also marked solvent effects on the separation of the non-equivalent methyl signals of the acac compounds.

Thus the number of bands observed, and the relative complexities of the spectra of the green compounds in non-donor solvents are fully consistent with a rigid non-planar salbn moiety. The complications from isomerism in many of the compounds were easily recognised and are themselves evidence for structure. Solvent effects and some accidental degeneracies cause complications; but overall the data unequivocally show that structure (II) is retained in these solutions.

Isomerism.—Geometrical isomers of the compounds with structure (II) can arise from two sources: (a) the non-equivalent substituent sites on the β-diketonate skeleton; and (b) the various non-equivalent positions which the methyl substituent can occupy in the salpn compounds. Thus for the unsymmetrical diketonates, there is the formal possibility of two isomers of the salen, four of the salbn, and eight of the salpn compounds (half this number for the symmetrical diketonates). From the known geometry of these molecules,[5] however, our calculations of intramolecular contacts of methyls in the four possible positions (VII) show that we can rule out the possibility of the salpn isomers for which the methyl occupies site 3 of structure (VII). The close contacts are listed in Table 2. Similarly, we can rule out half the formally possible isomers of the salbn compounds.

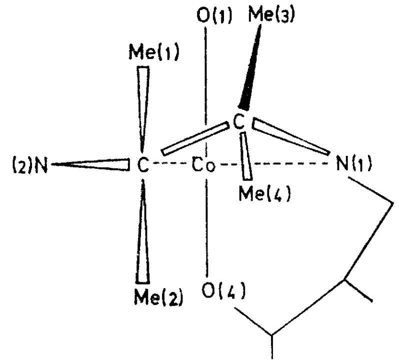
TABLE 2

Intramolecular contacts, less than 3·5 Å, of the possible methyls of the salpn compounds

Methyl [a]	Close contacts [b]	
1	C(17) 2·73	N(1) 2·46, C(26) 2·50
2	C(17) 3·27, C(24) 3·30, O(4) 3·47, N(2) 2·92	N(1) 2·46, C(26) 2·50
3	Co 3·29, O(1) 2·45 N(1) 3·03, C(1) 3·27, C(2) 2·95	N(2) 2·50, C(25) 2·53
4	C(24) 2·72	N(2) 2·50, C(25) 2·53

[a] These methyl positions refer to structure (VII). [b] In Å. The numbering system of the atoms is that of ref. 5. The first column gives those contacts which are dependent on conformation, whilst those in the second column are inherent in the basic ligand structure and are much the same in any conformation.

Most of the possible isomers have been detected in solution by the n.m.r. data (Table 3). The evidence comes mainly from the $CH_3(^1H)$ and $CF_3(^{19}F)$ resonances, with the latter being the most sensitive. In a few cases, there were non-integral intensities of some of the other ^1H resonances; but only for [Co(salpn)(tfacac)] in DMSO were separate signals observed for the γ-CH protons of the different isomers. For all compounds with sufficient solubility, the two isomers of the salen and salbn compounds, but only four of the six probable salpn isomers, have been positively detected.



(VII)

In our initial study of the isomerism, we had hoped to relate the solid and solution data; and, from a study of the isomer ratios, perhaps to infer something of the mechanism of the formation reaction. However, it is now clear that interconversion of isomers occurs in solution, probably in many cases through equilibria such as (1). The observed ratios of concentrations of isomers (Table 3) have no absolute significance, but merely indicate the ratio usually observed. Because of the difficulty of knowing which isomers are represented by the different n.m.r. signals, we have not attempted to define equilibrium values; nor have we studied the rates of interconversion, some of which would be measurable at normal temperatures.

*Other Spectroscopic Data.**—The *d–d* bands in the electronic spectra at *ca.* 16,000 cm^{-1}, which are often asymmetric, are consistent with but do not prove the octahedral structure. These bands move to lower energy, as expected, with increase in the electron-withdrawing power of the β-diketonate substituents. We have also observed, especially in the diffuse reflectance

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TABLE 3

A summary of the evidence for the isomerism of the green compounds in solution (n.m.r. data)

Compound	Solvent	Data [a]	Number of Isomers	Relative concentrations [b]
[Co(salen)(bzac)]	$(CD_3)_2SO$	^1H [Me]	2	1 : 4
[Co(salbn)(tfacac)]	$CDCl_3$	^1H [Me]	2	5 : 1
	$CHCl_3$	^{19}F [CF_3]	2	1 : 4
[Co(salbn)(tfta)]	$CHCl_3$	^{19}F [CF_3]	2	1 : 4
[Co(salpn)(acac)]	$CDCl_3$	^1H [pn-Me]	2	1 : 1·1 ⟶ 1 : 1·7 [d]
[Co(salpn)(bzac)]	$(CD_3)_2SO$	^1H [Me]	*e*	*e*
		^1H [pn-Me]	2	1 : 4
[Co(salpn)(tfacac)]	$CDCl_3$	^1H [Me]	2	5 : 1
		^1H [pn-Me]	2	1 : 2 [c]
	$CHCl_3$	^{19}F [CF_3]	4	1·3 : 1·9 : 5 : 1·9
	$(CD_3)_2SO$	^1H [Me]	2	5 : 1
		^1H [pn-Me]	2+ [f]	*f*
[Co(salpn)(tfta)]	$CHCl_3$	^{19}F [CF_3]	4	0·6 : 0·8 : 5 : 2·1
	$CDCl_3$	^1H [pn-Me]	2	1 : 1·44 ⟶ 1 : 2·0 [c,g]
	$(CD_3)_2CO$	^1H [pn-Me]	2	1 : 2·9

[a] Here we give, in brackets, the group which is the origin of the signal. [b] The lower field signal is given first. The figures are only an order of magnitude, based mainly on peak heights, with the exception of those marked with a *c*. [d] This is the range of observed intensities from seven different spectra. They were measured before it was appreciated that isomerisation was occurring, and the higher figure probably is nearest the equilibrium value. [e] The resonance was asymmetric to lower field. [f] The lower field signal was a multiplet, apparently arising from at least two overlapping doublets. Between 20 and 40 °C, this system is complicated by the presence of some [Co(salpn)(dmso)$_2$][tfacac], but above 50 °C, when this species is not detected, the signal still remains complex. Relative intensities, as defined in *a*, varied from 1 : 1 at 20 °C to 2 : 1 at 70 °C. [g] A sample collected from an Al_2O_3 column with $CHCl_3$ in six fractions gave the ratio 1 : 2·00 (±0·02) for each of these fractions. These solutions appear to represent the equilibrium mixture.

spectra (*cf.* ref. 10), spin-forbidden transitions at *ca.* 9 kK {$\varepsilon_{max.} = 1$ for [Co(salpn)(tfacac)] in $CHCl_3$}.

The i.r. spectra, which are the same for the solutions as for the solids, are evidence for the proposed structures.[4,11]

Some mass spectra were recorded in the hope that the fragmentation pattern might give structural data. However, parent peaks are generally quite weak, with the [Co(salrn)]$^+$ ion predominating, and there are few fragments readily observable between the two.

Rearrangements in Donor Solvents.—In donor solvents such as pyridine and DMSO, the compounds of tfacac, hfacac, tfta, sal, and ω-nap tend to react with solvent to give ionic species as in equilibrium (1) (where B = py or DMSO).

$$[\mathrm{Co(salrn)\,(X)}] + 2\mathrm{B} \rightleftharpoons \textit{trans}\text{-}[\mathrm{Co(salrn)(B)_2}]^+[\mathrm{X}^-] \quad (1)$$

Evidence for this includes isolation of compounds (Table), and the n.m.r., i.r., and electronic spectroscopic data.*

The ^{19}F spectra are invariably singlets; and the ^1H spectra were much simpler than those of the compounds in $CDCl_3$ or $(CD_3)_2CO$ (Figure 2). The singlets for the methylene protons of salen and salbn, and the CMe_2 protons of salbn are especially significant. Only a planar configuration of salrn will allow the rapid vibrations that make these protons equivalent. Note also the essential identity of the spectra of [Co(salen)(py)$_2$]X (where X = tfta and hfacac) in $CDCl_3$ and those of [Co(salen)X] dissolved in C_5D_5N.

We have looked at the n.m.r. data for evidence of

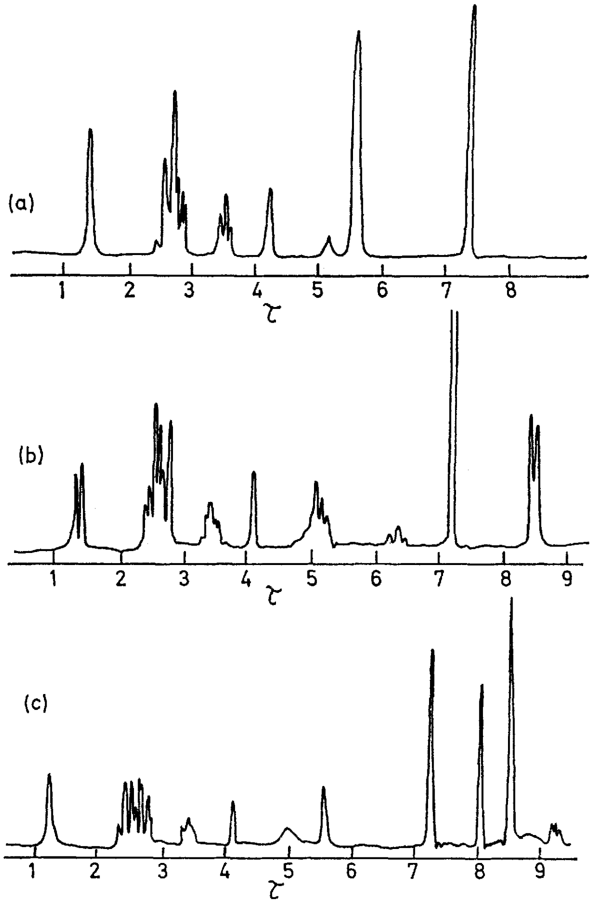

FIGURE 2 The ^1H n.m.r. spectra in C_5D_5N of (a) [Co(salen)(tfacac)], (b) [Co(salpn)(tfacac)], and (c) [Co(salbn)(tfacac)]. All compounds have rearranged in this solvent to the ionic species [Co(salrn)(py)$_2$][tfacac]

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* The Supplementary Publication No. SUP 20687 (24 pp., 1 microfiche) contains: (*i*) electronic spectra 30—5 kK; (*ii*) infrared spectra 1500—1800 cm^{-1}; (*iii*) mass spectra; (*iv*) ^1H n.m.r. spectra; and (*v*) ^{19}F n.m.r. spectra. For details of the Supplementary Publications scheme see Notice to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Index Issue.

[10] E. D. McKenzie, *J. Chem. Soc.* (*A*), 1969, 1655.

[11] J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 1965, 6740.

cobalt–carbon bonded species of type (III), but there is none. The spectra are quite different, for example, from those [2] of the compounds [Co(salrn){CH(CN)$_2$}L].

Rearrangements to ionic species also occur in DMSO solutions. For the hfacac compounds, the ^{1}H n.m.r. spectra detect only the ionic species; but for the tfacac and tfta compounds, the equilibrium (I) lies to the left, and the ^{1}H n.m.r. spectra show that only 10—20% of the compounds are present in the ionic form in these concentrated solutions and their concentration is inversely proportional to temperature. The ^{1}H n.m.r. spectra give no evidence for the presence of the ionic form of the acac, dbm, or bzac compounds, but here equilibrium (1) may provide a route for the interconversion of isomers (*q.v.*).

The brown solutions in pyridine have a featureless absorption extending over much of the visible region. The main *d–d* bands apparently have moved to higher energy, and are lost in the adjacent charge-transfer transitions.

General Comments.—Undoubtedly the main reason for the adoption of structure (II) is the formation of the β-diketonate chelate ring; and despite the strain [5] the compounds have a wide range of stability. Possible paths of decomposition found here are (i) the formation of the ionic species [Co(salrn)(solvent)$_2$]$^+$ [β-diketonate]$^-$ in donor solvents, and (ii) decomposition to the bis-terdentate species (IV).

With more rigidly planar ligands like saloph, the compounds do not appear to form, and in one case we have isolated [Co(bzac)$_3$] instead. However, even with the abpn, which is an unusual 'strong-field' planar N$_4$ ligand,[9] we have obtained a diamagnetic compound [Co(abpn)(tfta)], which appears to be of the same type.

One interesting result of this work has been the failure to obtain evidence for a *C*-bonded species of type (III); although, under conditions virtually identical to those used here, acetone forms [3] such a *C*-bonded species. This failure cannot be entirely a result of the greater stability of the bidentate species, since in donor solvents the diketones are ionised off from some of the compounds [equilibrium (1)], but they never seem to re-attach to the metal in a *C*-bonded mode (structure III).

We are indebted to Messrs. A. Cox, D. J. Mabbott, and G. A. Wright for some of the preparations, and to the S.R.C. for a studentship (to D. C.).

[2/1585 *Received, 5th July*, 1972]