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STRUCTURAL ASPECTS OF METAL COMPLEXES WITH SOME TETRADENTATE SCHIFF BASES

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CONTENTS

ABBREVIATIONS

bae	bis(acetylacetone)ethylenediiminate dianion
dmf	dimethylformamide
dmg	dimethylglyoximate ion
L	σ-donor ligand
M	metal
salen	bis(salicylaldehyde)ethylenediiminate dianion
3F-salen	bis(3-fluoro-salicylaldehyde)ethylenediiminate dianion

A. INTRODUCTION

Metal complexes of Schiff bases have been of considerable interest in the development of the inorganic chemistry of chelate systems[1,2].

Recently, metal complexes of some tetradentate Schiff bases such as bis(acetylacetone)-ethylenediimine and bis(salicylaldehyde)ethylenediimine have been intensively studied because of their unusual properties.

Many penta- and hexa-coordinate cobalt derivatives with stable σ Co–C bonds have been prepared and investigated[3]. Because of the stability of the σ Co–C bond and the overall physico-chemical behaviour of such compounds[4], they are studied as model molecules of the vitamin B_{12} group Of particular interest are the transmethylation reactions involving

TABLE 1

Complexes included in the survey

salen complex	Ref	salen complex	Ref	bae complex	Ref,
$[Co(salen)]_2$	10, 11	$[Fe_2(salen)_2O]$	19	[OV(bae)]	25
$[Co(salen)].CHCl_3$	12	$(ClFe(salen)]_2$	20	$[Cu(bae)]\ CH_3NH_3ClO_4$	26
[Co(salen).py]	13	[ClFe(salen)]	21	$[Cu(bae).H_2O]$	27
$[CH_3CH_2.Co(salen)]_2$	14	$[Cr(salen)(H_2O)_2]Cl$	22	$[Cu(bae)]\ ½H_2O$	28
$[Co_2(salen)_2.O_2\ (dmf)_2]$	15	$[Cu(salen)].CHCl_3$	23	$[C_6H_5.Co(bae)\ H_2O]$	29
$[(CH_3COCH_2)Co(salen)\ CH_3OH]$	16	$[Cu(salen)]\ p\text{-}HOC_6H_4NO_2$	24	$[CH_3\ Co(bae)]$	30
$[CH_3O\ Co(salen).py]$	16			$[CH_2{=}CH\ Co(bae)\ H_2O]$	31
$[CNCH_2.Co(salen)]_n$	16			$[Co(bae)].C_6H_6$	32
$[ClCo(salen)]_2$	17				
$[CH_2{=}CH.Co(salen)\ py]$	18				

TABLE 2

Analysis of bond lengths in salen complexes

Compound	M–O	M–N	C_1–O	C_7–N
[Co(salen)]$_2$	1 880(10)	1 880(10)	1 350(20)	1 310(20)
	1.950(10)	1 880(10)	1 340(20)	1 340(20)
[Co(salen)]$_2$	1 901(4)	1 886(5)	1 311(7)	1 301(8)
	1 940(4)	1 907(5)	1 325(7)	1 289(8)
[Co(salen)].$CHCl_3$	1 835(4)	1.829(5)	1.307(8)	1 286(9)
	1 869(5)	1 864(5)	1 302(7)	1 282(9)
[Co(salen) py]	1 900(10)	1 900(10)	1 360(20)	1 270(20)
[CH_3CH_2.Co(salen)]$_2$	1.901(5)	1 886(6)	1 315(9)	1 290(11)
	1.935(4)	1 880(6)	1.331(9)	1 279(11)
[Co_2(salen)$_2$ O_2 (dmf)$_2$]	1 900(5)	1 894(7)	1 323(11)	1 302(12)
	1 903(6)	1 872(6)	1.313(10)	1 282(13)
[(CH_3COCH_2)Co(salen)CH_3OH]	1 918(8)	1 909(10)	1 275(15)	1 254(16)
	1 909(8)	1 860(10)	1 303(13)	1.280(16)
[CH_3O Co(salen) py]	1 894(8)	1 904(10)	1 339(14)	1 304(17)
	1 907(8)	1 906(10)	1 343(14)	1 333(14)
[$CNCH_2$.Co(salen)]$_n$	1 893(11)	1 880(13)	1.278(16)	1 307(16)
	1 907(11)	1 889(11)	1 305(16)	1 290(16)
[ClCo(salen)]$_2$	1 889(10)	1 903(10)	1 292(20)	1 289(20)
	1 937(10)	1 884(10)	1.320(20)	1 310(20)
[CH_2=CH Co(salen) py]	1 879(7)	1 860(8)	1.319(11)	1 264(15)
[Fe_2(salen)$_2$O]	1 915(16)	2 089(18)	1 320(30)	1 230(30)
	1 953(17)	2 112(18)	1 370(30)	1 300(30)
	1 919(17)	2 087(21)	1.310(40)	1 280(30)
	1 886(17)	2 059(20)	1 350(30)	1 270(30)
[ClFe(salen)]$_2$	1 898(7)	2 098(9)	1 337(12)	1 252(13)
	1 978(7)	2 091(10)	1 352(11)	1 314(14)
[ClFe(salen)]	1 879(10)	2 099(11)	1 329(16)	1.317(17)
	1 885(11)	2 064(10)	1 365(16)	1.314(17)
[Cr(salen)(H_2O)$_2$]Cl	1.916(8)	2 005(9)	1 336(13)	1.294(14)
	1 951(8)	1 997(8)	1 344(16)	1 296(14)
[Cu(salen)] $CHCl_3$	1 920(9)	1 930(9)	1 330(16)	1 270(16)
	1 900(9)	1 950(9)	1 320(16)	1.290(16)
[Cu(salen)] *p*-$HOC_6H_4NO_2$	1.906(9)	1 928(9)	1.340(18)	1 310(18)
	1 886(9)	1 904(9)	1.320(18)	1.310(18)
Weighted average.(*A*)	1 904(6)	1 912(12)	1 321(3)	1 291(3)
Range	0.143	0 283	0 095	0.110

Compound	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5
$[Co(salen)]_2$	1 410(20)	1 380(20)	1 390(30)	1.370(20)
	1.420(20)	1.430(20)	1 360(20)	1 380(20)
$[Co(salen)]_2$	1 426(10)	1.399(10)	1 421(12)	1.379(11)
	1.419(9)	1 399(10)	1 410(12)	1.390(12)
$[Co(salen)].CHCl_3$	1 414(10)	1.368(11)	1.402(13)	1 346(12)
	1.397(9)	1.356(10)	1 357(11)	1.364(12)
[Co(salen).py]	1 400(20)	1 410(20)	1.380(30)	1 390(30)
$[CH_3CH_2.Co(salen)]_2$	1.413(11)	1.382(13)	1.395(12)	1.358(13)
	1.409(11)	1 394(13)	1.363(13)	1 363(13)
$[Co_2(salen)_2.O_2(dmf)_2]$	1 418(11)	1.404(14)	1 376(14)	1.373(12)
	1 402(13)	1 398(15)	1 410(14)	1 354(14)
$[(CH_3COCH_2)Co(salen)CH_3OH]$	1.440(19)	1 416(18)	1 418(23)	1.367(22)
	1.433(18)	1.387(19)	1 437(21)	1.363(21)
$[CH_3O.Co(salen).py]$	1 416(17)	1 395(19)	1 447(21)	1 354(19)
	1.446(16)	1.408(17)	1 419(17)	1 428(16)
$[CNCH_2.Co(salen)]_n$	1 413(19)	1 376(17)	1 436(24)	1 375(23)
	1.397(18)	1.340(19)	1 422(21)	1 348(22)
$[ClCo(salen)]_2$	1.400(20)	1 385(30)	1 365(30)	1 371(30)
	1.412(20)	1 405(30)	1.365(30)	1 339(30)
$[CH_2=CH.Co(salen).py]$	1.408(14)	1.366(15)	1.375(20)	1.352(19)
$[Fe_2(salen)_2O]$	1 370(30)	1.410(40)	1 410(40)	1 380(40)
	1 430(30)	1 420(40)	1.340(40)	1 390(40)
	1 400(40)	1 410(40)	1.420(40)	1 430(40)
	1 480(40)	1 390(40)	1 350(40)	1.370(40)
$[ClFe(salen)]_2$	1 395(17)	1 382(17)	1 417(20)	1 386(19)
	1 391(17)	1 394(16)	1 367(20)	1 367(20)
[ClFe(salen)]	1.414(18)	1.360(24)	1 410(22)	1.415(28)
	1 477(27)	1.345(23)	1 398(21)	1 357(21)
$[Cr(salen)(H_2O)_2]Cl$	1 409(16)	1.391(18)	1 407(18)	1.384(18)
	1 399(16)	1.396(16)	1.378(21)	1 403(20)
$[Cu(salen)].CHCl_3$	1 410(20)	1.380(20)	1 390(20)	1.370(20)
	1.400(20)	1 410(20)	1 390(20)	1.380(20)
$[Cu(salen)].p\text{-}HOC_6H_4NO_2$	1 410(23)	1.420(23)	1.370(23)	1 370(23)
	1.380(23)	1 400(23)	1.430(23)	1 370(23)
Weighted average	1 412(3)	1 389(4)	1 395(4)	1 372(3)
Range	0.110	0 090	0 107	0 091

C_5-C_6	C_6-C_7	C_8-C_9	C_1-C_6	C_8-N	Ref.
1 450(20)	1 390(20)	1 530(20)	1.430(20)	1.460(20)	10
1 470(20)	1 430(20)		1.370(20)	1 450(20)	
1.426(9)	1.432(10)	1 525(10)	1.438(10)	1.484(8)	11
1.430(9)	1 462(10)		1.410(9)	1.477(8)	
1 398(10)	1.436(10)	1.442(13)	1.399(9)	1.498(10)	12
1.406(10)	1 406(10)		1.424(7)	1.476(10)	
1 450(20)	1.440(20)	1 440(30)	1 420(20)	1.480(20)	13
1.433(12)	1.432(11)	1 531(9)	1.420(10)	1.469(9)	14
1.429(12)	1 443(11)		1.411(10)	1 483(10)	
1.432(13)	1 420(11)	1 532(14)	1.428(12)	1.473(10)	15
1.429(13)	1.432(12)		1.430(12)	1.460(10)	
1 422(18)	1 436(19)	1 587(21)	1 439(20)	1 507(17)	16
1 404(19)	1 438(19)		1 439(18)	1.498(17)	
1 402(17)	1 432(17)	1.515(19)	1.432(16)	1.480(19)	16
1 438(16)	1 451(16)		1.404(15)	1 482(18)	
1.421(18)	1 407(21)	1 485(19)	1 442(20)	1.484(20)	16
1 429(19)	1 450(20)		1 423(18)	1 499(18)	
1.389(30)	1 387(30)	1.537(30)	1 420(30)	1.461(20)	17
1.434(30)	1 433(30)		1 414(30)	1 498(20)	
1 432(15)	1 411(15)	1 520(28)	1.398(15)	1.440(22)	18
1 430(40)	1 420(30)	1 510(30)	1.370(30)	1 500(30)	19
1 380(30)	1 480(40)		1 350(30)	1.500(30)	
1 410(30)	1 520(30)	1 570(40)	1 370(30)	1 470(30)	
1 430(40)	1 400(30)		1.420(30)	1.500(30)	
1 428(16)	1 436(17)	1 496(16)	1.408(17)	1 516(16)	20
1 409(15)	1 449(17)		1 399(17)	1.498(16)	
1.430(21)	1.449(19)	1 620(20)	1.431(21)	1 472(19)	21
1.424(17)	1.434(20)		1.400(19)	1 481(20)	
1 410(17)	1.433(16)	1.518(16)	1.403(14)	1.484(14)	22
1 396(17)	1.453(16)		1 424(15)	1.468(16)	
1 410(20)	1 440(20)	1.500(20)	1.390(20)	1.500(16)	23
1 440(20)	1.430(20)		1.420(20)	1 480(16)	
1.410(23)	1 430(23)	1.490(23)	1 380(23)	1.460(16)	24
1 430(23)	1.450(23)		1 430(23)	1 510(16)	
1 422(3)	1 434(3)	1 510(11)	1 416(3)	1.481(3)	
0.090	0.133	0 188	0 092	0 066	

TABLE 3

Analysis of bond lengths in bae complexes

Compound	M–O	M–N	C–O	C_4–N
[OV(bae)]	1 945(7)	2 059(9)	1 305(12)	1.292(14)
	1 956(8)	2.048(8)	1 294(13)	1 298(14)
[Cu(bae)].$CH_3NH_3ClO_4$	1 900(8)	1.930(8)	1.310(15)	1 320(15)
	1.940(8)	1.930(8)	1 290(15)	1 300(15)
[Cu(bae) H_2O]	1 929(3)	1 950(4)	1.286(6)	1 303(6)
	1.928(3)	1.952(4)	1 292(5)	1.300(6)
[Cu(bae)] ½H_2O	1 914(10)	1.916(10)	1.300(20)	1 340(20)
	1 926(10)	1 922(10)	1 350(20)	1 330(20)
[C_6H_5Co(bae) H_2O]	1.910(10)	1.890(20)	1 290(30)	1 360(30)
[CH_3 Co(bae)]	1.874(11)	1.860(13)	1 313(19)	1 342(20)
	1 871(11)	1 870(12)	1 266(19)	1 318(21)
[CH_2=CH Co(bae) H_2O]	1 913(7)	1 888(8)	1 301(13)	1.318(13)
	1 930(7)	1 892(8)	1 290(12)	1 299(13)
[Co(bae)] C_6H_6	1.854(11)	1 864(12)	1 304(17)	1.354(19)
	1 852(9)	1 884(13)	1 297(16)	1 330(19)
Weighted average (A)	1 922(6)	1 941(13)	1 294(3)	1.308(4)
Range	0 104	0 195	0 084	0 068

these complexes[5] Furthermore the property of Co(salen) to absorb reversibly molecular oxygen has been known for many years[1]. Recently, some oxygen adducts of formula [Co(salen)]$_2(O_2)L_2$ have been isolated and studied[6] Finally, evidence for the existence of some oxygen adducts of formula Co(salen)(O_2)L (refs 7, 8) and Co(bae)(O_2)L (ref. 9) has been reported

In view of the considerable number of X-ray diffraction structural determinations of salen and bae complexes, carried out both in our laboratory and in others (see references of Table 1) and the particular importance of the structural results to clarify the chemical properties of these compounds, it seems appropriate to summarize these data and to point out some interesting features which they suggest Table 1, which covers the literature until 1970, lists the complexes which have been included in this survey.

B. INTERATOMIC DISTANCES

Interatomic distances for salen and bae complexes are listed in Tables 2 and 3, compiling the two values for each chemically equivalent distance. The labelling of atoms is shown in Fig. 1. The range of each distance, together with the calculated average values (A) with their standard deviation (σ_A) in parentheses, is also reported The averages were calculated by weighting each measurement of all the available three-dimensional determinations by the

C_6–N	C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_6–C_7	Ref
1 505(19)	1.487(16)	1.373(16)	1.391(17)	1.480(19)	1.421(21)	25
1 512(15)	1 497(20)	1.359(16)	1.389(16)	1.534(17)		
1 430(15)	1 510(18)	1.330(18)	1 420(18)	1.480(18)	1.480(18)	26
1.450(14)	1 560(18)	1.330(18)	1.470(18)	1 490(18)		
1.450(6)	1 522(7)	1 375(7)	1.423(7)	1.521(7)	1 508(8)	27
1 455(7)	1 532(7)	1 380(8)	1 433(8)	1.515(8)		
1.480(20)	1 540(30)	1 380(30)	1 380(30)	1.530(30)	1 430(30)	28
1.460(20)	1.540(30)	1 350(30)	1 390(30)	1 560(30)		
1.500(30)	1 530(30)	1.380(30)	1 400(30)	1.470(30)	1.590(30)	29
1 453(23)	1 498(28)	1.325(23)	1 387(24)	1 611(25)	1.516(26)	30
1 494(23)	1 560(24)	1.329(24)	1.430(25)	1 513(26)		
1 476(15)	1 518(17)	1 357(15)	1 423(16)	1 517(16)	1 528(14)	31
1.466(13)	1 508(15)	1 389(15)	1.458(15)	1.512(17)		
1.484(22)	1.494(28)	1 338(23)	1 420(26)	1.523(22)	1 513(20)	32
1.494(20)	1 519(22)	1 368(24)	1 409(24)	1 534(26)		
1.462(5)	1 523(4)	1.366(5)	1.423(6)	1 517(6)	1.503(12)	
0.082	0 073	0.064	0.090	0 141	0.169	

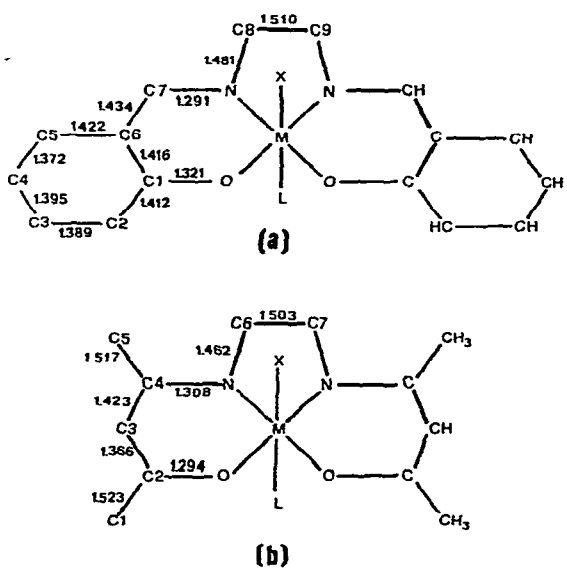

Fig 1 Numbering scheme and average bond lengths for (a) salen and (b) bae metal complexes

inverse square of its individual standard deviation. No two-dimensional determination has been taken into account, because such results can involve very large errors.

(i) Metal–ligand bond lengths

Comparison of σ_A values of the metal–salen bond lengths with individual σ determinations shows variation of these distances among the compounds examined, as would be expected for different metal atoms. The influence of the nature of the metal is clearly illustrated by the following trend of the mean values of the metal–nitrogen bond lengths in salen complexes Co–N, 1.884 Å; Cu–N, 1.928 Å, Cr–N, 2 001 Å; Fe–N 2 087 Å. However, significant differences also appear in complexes containing the same metal atom. This can arise from the different kind of coordination and/or from extra bond formation of the coordinated oxygen atoms. In fact a significant lengthening of the Co–O distance is observed where the oxygen atom is coordinated to the metal atom of another M(salen) unit to give dimeric molecules $[M(salen)]_2$ or when it is involved in hydrogen bonds.

It must be emphasized that no significant difference is observed in Co–O(N) distances with the same metal in different formal oxidation states.

Perhaps because of the last two effects, no trend in the metal–oxygen bond lengths can be observed. Since few examples are available for different coordination types with the same metal, it is difficult at present to correlate bond lengths with different stereochemistry. However, it seems that the coordination bond lengths in the tetracoordinate Co(salen) are significantly shorter than in the other compounds

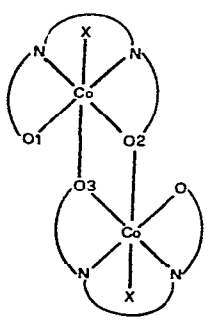

Fig 2 A sketch of dimeric Co(salen) compounds

Examination of the axial bond lengths shows strong evidence of *trans* influence in the octahedral cobalt compounds[14]. For the dimeric $[XCo(salen)]_2$ complexes in which an oxygen atom of a Co(salen) moiety is bonded to the cobalt atom of the other moiety, the Co–O(3) distance is 2 342(3) Å when X = CH_2CH_3 (ref. 14) and 1 995(13) Å when X = Cl (Fig 2) and the differences between Co–O(1) and Co–O(2) distances are 0.048 and 0.034 Å

respectively. In the oxygen adduct of Co(3F-salen)[33] the Co–O(3) distance is 2 193 Å when X = O_2 and the difference between Co–O(1) and Co–O(2) bond lengths is 0.087 Å, however, these values have to be considered with some care because of the low accuracy of this structure determination (R = 0 15)

The values reported above seem indicative of some charge transfer in the cyclic CoO(3)O(2)Co group influenced by the nature of the X ligand

Further evidence of *trans* influence in octahedral salen compounds arises from comparison of the Co–N bond lengths *trans* to $-OCH_3$ (ref 16), $-CH_2CN$ (ref. 16) and $-CH{=}CH_2$ (ref 18) groups, which assume the values 2.031(9), 2 092(17) and 2 119(10) Å respectively, and from comparison of the Co–O distances *trans* to $-O_2$ (ref 15) and to $-CH_2COCH_3$ (ref 16), their values being 2 150(7) and 2 202(9) Å respectively The trend in these bonds lengths is to increase with increasing ratio $S^2/\Delta E$ (Table 4), where S is the overlap integral between, and ΔE the absolute separation in energy of, the interacting orbitals. In fact from perturbation theory this ratio may be taken as a measure of the strength of a bond and, as recently proposed, may be assumed to be related to the *trans*-influencing ability of a ligand in square planar[34] or octahedral complexes[35].

TABLE 4

Relation between Co–O(N) distances and the quantity $S^2/\Delta E$★ of the *trans*-influencing ligands

Compound	Bond	*Trans*-ligand	$S^2/\Delta E$ ($eV^{-1} \times 10^{-2}$)	Distance (Å)
[CH_3O.Co(salen) py]	Co–N	–O	<0 9	2 031 (9)
[$NCCH_2$.Co(salen)]$_n$	Co–N	–C (sp^3)	1 4	2 092 (17)
[CH_2=CH Co(salen) py]	Co–N	–C (sp^2)	1 5	2 119 (10)
[Co_2(salen)$_2$.O_2 (dmf)$_2$]	Co–O	–O	<0 9	2 150 (7)
[CH_3COCH_2 Co(salen) CH_3OH]	Co–O	–C (sp^3)	1 4	2 202 (9)

★Data from ref 35

Finally, the Co–C σ-bond lengths of the organometallic derivatives are 1 990(7) Å in Co–CH_2CH_3 (ref. 14), 1 988(22) Å in Co–CH_2CN (ref 16), 2.019(14) Å in Co–CH_2COOCH_3 (ref. 16) and 1.93 Å in Co–$CH{=}CH_2$ (ref. 18). Whereas the first three values are similar (mean value 1 999 Å), the Co–C distance in the vinyl derivative appears significantly shorter, even after correction for different carbon σ-covalent radii.

The variations in the M–O and M–N distances in bae complexes are similar to those of salen derivatives However, because dimeric species have not been found in the compounds examined, the M–O bonds are affected only by hydrogen bonding in some cases, and this provokes a negligible lengthening of the M–O distances. In fact neglecting the hydrogen bonding effect and the different coordination type, the following average values are obtained.

Co–O 1 886 Å	Co–N 1.881 Å
Cu–O 1.923 Å	Cu–N 1.933 Å
V–O 1 951 Å	V–N 2 054 Å

The variation in the M–O distances follows the same order as the metal–oxygen distances in the corresponding acetylacetonate compounds[36].

Making allowance for the different σ-covalent radii of the hybridized carbon atom, the values of the σ cobalt–carbon bond lengths are 1 91 Å for the Co–$CH{=}CH_2$ group[31], 1.95 Å for the Co–C_6H_5 group[29] and 1.95 Å for the Co–CH_3 group[30].

We must note that comparison of Co–C distances in bae and salen organocobalt derivatives suggests evidence of *cis* influence In fact the Co–alkyl distance of 1.999 Å in salen compounds seems significantly longer than the value of 1 95 Å in bae compounds. This difference is only ascribable to the different nature of the equatorial ligand, because the *trans* influence of the ligands *trans* to carbon atom is very similar, as shown by the values of the Co–C bond lengths in compounds with the same equatorial ligand.

(ii) Bond lengths of the tetradentate ligands

The mean values and σ_A of the salen ligand bond lengths have been calculated for all the available complexes and for the cobalt complexes alone, the same values are obtained

Furthermore, since the σ_A values (see Table 2) are three to five times less than the σ of an individual determination, it can be assumed that the ligand bond lengths are independent of the nature of the metal The mean values are also reported in Fig. 1(a). They agree very well with those reported by Lingafelter and Braun[36] for the salicylaldiminate group The difference in the C–C bond lengths between the 'near' and 'far' sides (with respect to the metal atom) of the benzene ring is similar to that previously observed for the salicylaldiminate ligand. These differences are significant and do not seem ascribable to librational motions. Indeed the bond lengths corrected for the rigid body motion of molecules according to Schomaker and Trueblood[37] follow the same trend in the same molecule. Bond length correction was applied using a programme written by Filippini and Gramaccioli[38]. Furthermore, as shown by Lingafelter and Braun[36], the values of the bond lengths in the benzene ring may be explained on the basis of calculations using the simple Huckel MO method applied to the π-electron system of the salicylaldiminate ion.

It may also be assumed for the bae ligand that the bond lengths are independent of the nature of the metal (see Table 3 and Fig 1(b)). An interesting feature is that the C(3)–C(2) and C(3)–C(4) distances are not equivalent, the latter being significantly longer. This result is in agreement with the calculated π-overlap populations evaluated by the EHMO method[39] The C(1)–C(2) and C(4)–C(5) distances of 1 517(6) and 1 523(4) Å have the value expected for a carbon (sp^3)–carbon (sp^2) bond length On the other hand, the CH_2–CH_2 bond length of 1 503(12) Å is shorter, both in salen and in bae, than the value expected for a C(sp^3)–C(sp^3) bond However, the discrepancy may not be significant owing to the high value of the corresponding σ_A

It is interesting to observe that the mean value of the C—O distance in the salen complexes is longer than the corresponding distance in bae complexes, whereas the N—C distance in the former ligand is shorter

C. CONFORMATIONAL ASPECTS

In the octahedral complexes the salen ligand can act both as tetradentate and as a bis-bidentate ligand[40] In the first case two different arrangements of the four donor atoms around the metal atom have been found, one in which the donors occupy the four equatorial positions, the other in which one oxygen is displaced from the equatorial plane, occupying an axial position of the coordination polyhedron[40,41] (Fig 3).

In the tetra- and penta-coordinate complexes so far examined, the salen ligand has been always found with the conformation sketched in Fig. 3(a). Some conformational data of salen complexes in the latter geometrical arrangement are shown in Table 5

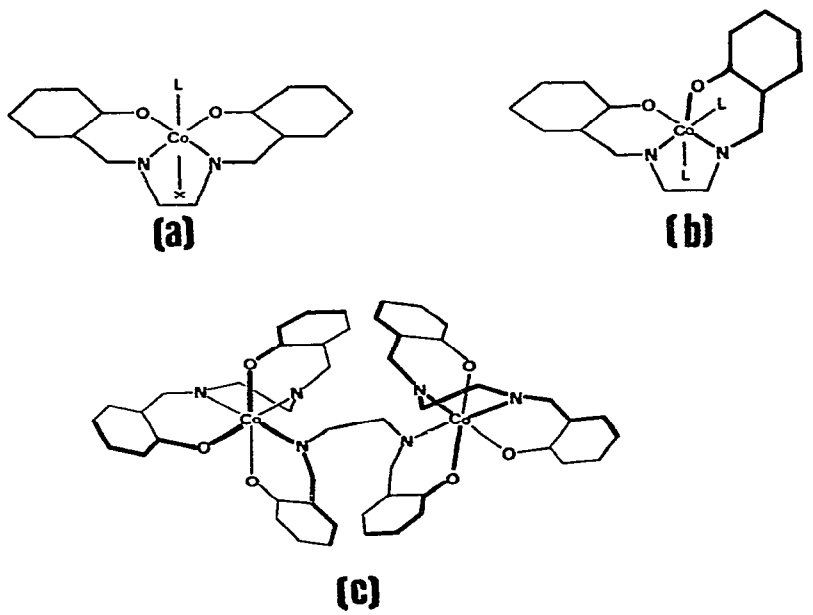

Fig 3 Possible arrangements of salen as (a) and (b) a tetradentate ligand and (c) a bis-bidentate ligand

The four donor atoms are almost always coplanar with small deviations towards a tetrahedral geometry, as indicated by the values of their deviation from the equatorial plane and by the 'torsional' angle $\widehat{NOON}$ as shown in the first two columns of Table 5 The iron complexes show the most significant deviations from planarity when compared with those of cobalt and copper. In the third column of Table 5 the displacements of metal

TABLE 5

Some conformational data for salen complexes

Compound	$O_1O_2N_1N_2$ (Å)	NOON (angle in degrees)	d (Å)		α (°)	β (°)	γ (°)	d_1 (Å)	d_2 (Å)	φ (°)
$[Co(salen)]_2$★	0 042	1.7	0 132	stepped	2 4	26.1	23.6	−0 37	0 19	38.7
$[Co(salen)].CHCl_3$	0 050	2 2	0 003	planar	1.5	4 3	4.5	−0 11	−0 03	10.8
[Co(salen).py]	0	0	0 200	umbrella	14 4	14 4	28.8	0 05	0 05	0
$[CH_3CH_2.Co(salen)]_2$	0 031	1 2	0 058	stepped	7 5	25 1	17 5	−0 47	0 14	44 0
$[Co_2(salen)_2\ O_2.(dmf)_2]$	0.017	0 7	0 064	stepped	4 1	24.2	20 1	−0.32	0 25	39.5
$[(CH_3COCH_2)Co(salen)CH_3OH]$	0 036	1 5	0 082	stepped	7 2	11 2	5.5	−0 45	0.14	37 9
$[CH_3O.Co(salen).py]$	0 080	3 2	0 008	umbrella	4 0	15 5	17 0	−0 40	0 27	43.0
$[CNCH_2.Co(salen)]_n$	0 020	0.8	0 010	umbrella	2 1	20.2	22.3	−0.49	0	34.6
$[CH_2{=}CH.Co(salen)\ py]$	0	0	0.015	umbrella	8 4	8 4	16 8	−0 28	0 38	44 0
$[Fe_2(salen)_2O]$	0.400	15 7	0 570	umbrella	19 7	21.4	41.0	−0 42	0 36	40.3
	0 200	7 9	0 549	umbrella	9 9	15.8	24.1	−0 46	0.32	44.8
$[ClFe(salen)]_2$	0.070	2 5	0.170	stepped	8 9	30 4	21.5	−0.45	0 16	47 4
[ClFe(salen)]	0 220	9.1	0 490	umbrella	6.5	14 9	19.4	−0.38	0 40	43 7
$[Cr(salen)(H_2O)_2]Cl$	0 082	3 2	0 077	stepped	11 6	28 3	17 0	−0 38	0 27	46 8
$[Cu(salen)],CHCl_3$	0.067	2.7	0 049	stepped	6 5	16.9	12 1	−0.44	0 12	41 3
$[Cu(salen)].p\text{-}HOC_6H_4NO_2$	0 108	4 4	0 032	planar	2 1	5.1	4.5	−0 28	0.20	30 2

★Data from ref 11

atoms from the coordination plane are given The values of the out-of-plane distances are mainly influenced by the nature of the metal and the kind of coordination. They are in fact markedly greater for the iron compounds and for the pentacoordinate stereochemistry. It is interesting to note that similar displacements of the iron atom have been found in the iron porphine (0 38 Å in chloroirontetraphenylporphine[42] and 0 20 Å in aquohydroxyirontetraphenylporphine[43]) and iron porphyrin derivatives (0 475 Å in chlorohaemin[44] and 0 455 Å in methoxyironmesoporphyrin-IX-dimethylester[45]) On the other hand, the cobalt atom lies almost in the coordination plane as also found in vitamin B_{12} (0 05 Å in air-dried crystals[46] and 0 04 Å in wet crystals[47]).

Three conformations of the salen ligand(Fig. 3(a)) are observed, as shown in the fourth column of Table 5 The ligand in the tetracoordinate complexes is very nearly planar, whereas umbrella-shape and stepped-shape conformations seem to be preferred in penta- and hexa-coordinates species. The last two cases are illustrated in Fig. 4. They are described by the angles α and β between the coordination plane and the planes defined by the two salicylaldimine residues and the angle γ between the last two planes For a planar conformation $\alpha = \beta = \gamma = 0$, for the umbrella-shape conformation $\gamma = \alpha + \beta$ and for the stepped one $\beta = \alpha + \gamma$ These relations are only approximate because of some twisting of the above planes

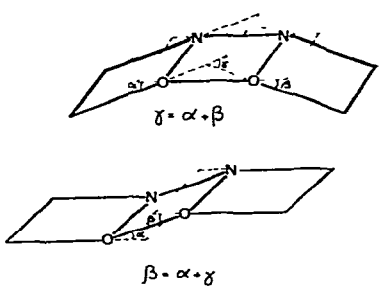

Fig 4 Salen ligand umbrella-shape and stepped-shape conformations

Data reported in the last column of Table 5, where displacements d_1 and d_2 of ethylene carbon atoms from the coordination plane and the torsional angle φ around the CH_2—CH_2 bond are reported, suggest a qualitative interpretation of the possible conformations of the five-membered ring containing the ethylene bridge. A symmetric stepped arrangement of the molecule causes a symmetrical displacement of the ethylene carbon atoms above and below the coordination plane, favouring a 'half-chair' (*gauche* conformation of the ethylene bridge) conformation of the ring[19]. A symmetric umbrella-shape arrangement leads to an 'envelope' conformation (*cis* conformation of the ethylene bridge). As can be seen by inspection of molecular models, the trigonal nature of the bonds of the imine nitrogen atoms is retained, as suggested by the sum of bond angles around these atoms which is very close to 360° However, if neither arrangement of the molecule is symmetrical (i e. $\alpha \neq \beta$

for umbrella and $\alpha \neq \gamma$ for stepped case) a 'half-chair' conformation again arises, but the ethylene carbon atoms are asymmetrically displaced from the coordination plane. This may be summarized in the scheme

symmetric stepped ——————→ half-chair (symmetric)
symmetric umbrella ——————→ envelope
asymmetric stepped ——————→ half-chair (asymmmetric)
asymmetric umbrella——————→ half-chair (asymmetric)

Obviously it may happen that a simultaneous asymmetric bending and twisting of the two halves of the salen ligand can produce a more symmetric displacement of the carbon atoms than expected

Although isomers of *cis*-$(NH_3)_2$Co(bae) in which the four donor atoms of bae do not lie in the same plane[1] have been isolated, no X-ray data have been obtained so far for such an arrangement In fact in the complexes examined by X-ray analysis the ligand is always found to be planar or nearly planar Table 6 reports some significant data on the conformation of bae compounds The values listed have the same meaning as the corresponding columns in Table 5 γ is the angle between the two planes passing through the two chemically equivalent halves of the ligand

Inspection of Table 6 shows that the bae ligand can exist in strictly planar, asymmetric umbrella-shaped and distorted conformations Like salen complexes, the tetracoordinate compounds seem to prefer a planar geometry with the metal in the plane of the donor atoms, whereas in the hexa- and penta-coordinate compounds significant deviations from planarity are observed It is worthwhile to note that in the penta-coordinate species the metal atom is more displaced from the basal plane towards the apical ligand than it is from the equatorial plane in the hexacoordinate complexes.

Regarding the other conformations illustrated in Fig 3, too few accurate structural data are available for a comparison However, it may be stated that planarity of the two salicylaldimine residues is again maintained. In the complexes of Fig 3(b), the ring ethylene bridge has an approximately 'half-chair' conformation, whereas in the bis-bidentate salen ligand the ethylene bridge adopts an exact *trans* conformation[40].

D DISCUSSION

Salen and bae ligands have a strong tendency towards planarity, as shown from the structural determinations of tetracoordinate complexes Such a tendency may be explained together with the values of the ligand bond lengths, in terms of π-electron delocalization on the tetradentate ligand, delocalization which is independent of the nature of the metal atom. The deviations from planarity observed in hexa- and penta-coordinate species are to be attributed to interactions of the bae and salen ligands with axial (or apical) ligands, as confirmed by the fact that the more bulky are the latter, the larger are the distortions in the tetradentate ligands[13].

TABLE 6

Some conformational data for bae complexes

Compound	$O_1O_2N_1N_2$ (Å)	NOON (angle in degrees)	d (Å)		γ (°)	d_1	d_2	φ (°)
[OV(bae)]	0.180	6.1	0 580	umbrella	35 3	0.34	−0 02	21 7
[Cu(bae)] $NH_3CH_3ClO_4$	0	0	0	planar	0	0	0	0
[Cu(bae).H_2O]	0.042	1 7	0 138	umbrella	11 8	−0 11	−0.15	4 1
[Cu(bae)].½H_2O	0.102	4 2	0.005	nearly planar	3 5	−0 11	0 10	11 7
[Co(bae).C_6H_5.H_2O]	0 020	0.8	0 112	umbrella	8 9	0 31	−0.21	32.9
[CH_3.Co(bae)	0.018	0.8	0 118	nearly planar	4 0	0 15	0 11	2 2
[CH_2=CH.Co(bae).H_2O]	0 015	0 6	0 060	distorted	11.2	0 17	−0 42	42.6
[Co(bae)].C_6H_6	0	0	0	planar	0	0	0	0

The coordination bond lengths involving the equatorial ligand are particularly short for cobalt compounds and independent of the formal oxidation state of the metal, whereas Co^{II}–N(O) and Co^{III}–N(O) σ-bond lengths are usually found to vary significantly. For example, Co–N (peptide) ranges from 2.12–2 14 Å and Co–O from 2 07–2.15 Å in bis-L-histidinate Co^{II} H_2O (ref 48) and DL-histidinate Co^{II} $2H_2O$ (ref 49) Co–N (peptide) is 1 87 Å and Co–O ranges from 1 93–1 98 Å in bis(glycylglycinate) Co^{III} (ref. 50) The observed phenomenon may be interpreted assuming a π-bonding contribution between the metal and the tetradentate ligand, the amount of π-bonding depending on the oxidation state of the metal Such a model is consistent with the redox properties of cobalt chelate systems[51]

It seems likely that this participation of the metal atom electrons in delocalized π-orbitals is mainly responsible for the ability of Co(salen)-type compounds to form stable σ-cobalt–carbon bonds and to bind reversibly molecular oxygen As previously reported[52], both these properties are strictly related, depending upon the orbital arrangement of the metal atom However, whereas both penta- and hexa-coordinate species of Co(salen) and Co(bae) form stable σ –Co–C bonds, for stabilization of the Co–O_2 bond in oxygenated forms, bonding of a *trans* σ-donor seems indispensable since oxygenation can occur only in the presence of σ-donor ligands[6–9]

The influence of different equatorial ligands on the cobalt atom has been studied by means of polarographic techniques[51] The trends of the half-wave potentials of the Co^{III}–Co^{II} and Co^{II}–Co^{I} couples in salen, bae and dmg complexes show an increase of electron affinity of the oxidized form in passing from salen to dmg. The different electron situation of the metal atom with different chelate systems is reflected in different structural aspects of these complexes For example, the order of increasing *cis* influence in the organo-cobalt derivatives is dmg > salen > bae In fact, the mean values of the Co–C bond length are 2 04 (ref 53), 2 00 and 1 95 Å respectively Similar trends have been observed for other aspects of physico-chemical behaviour of these complexes, such as the ground-state and thermodynamic *cis* effect[4]

The shorter Co–C distances in vinyl salen and bae derivatives seem to indicate some π-bonding contribution to the total bond order of the Co–C bond, which significantly affects this distance

Another important difference arises from the ability of salen derivatives to give dimers, whereas such species have not so far been obtained for the bae derivatives. This could be related to the different electron arrangement of the metal atom induced by the different equatorial ligands However, the main reason seems to lie in the nature of the ligand itself, as shown by comparison of the O–C and N–C bond distances, which, as already observed,

are independent of the nature of the metal. The mean value of the O–C bond length in salen derivatives is greater (1.321 ± 0 003 Å) than that found in bae compounds (1.294 ± 0.003 Å), whereas the N–C bond length is greater in the latter ligand (1.308 ± 0 004 Å) than in salen (1 291 ± 0.003 Å) These values are in agreement, as previously proposed[14], with a lesser bond order in the O–C bond of the salen ligand than in that of bae, the reverse being observed for the N–C bonds. The same conclusions may be derived from the calculated π-overlap populations of the O(N)–C bonds[39] Thus the ability of salen complexes to form dimeric molecules could derive from the greater availability of $2p_z$ orbitals on oxygen atoms (the z-axis is taken perpendicular to the x,y plane of the tetradentate ligand) which can form a further σ-bond with the cobalt atom of another Co(salen) unit Moreover, a weakening of the Co–O(2) bond (see Fig 2) results. The importance of the nature of the equatorial ligand in determining the ability to dimerize is also illustrated by the fact that even hydrogen bonding involving the coordinated O(2) atom can substantially alter this ability, e g in Cu–salen complexes. Whereas in Cu(salen)[54] there is dimer formation, in the chloroform and p-nitrophenol adducts the Cu–O(2) distance increases with increasing hydrogen bond strength until no dimerization occurs in the latter compound On the other hand, Van der Waals forces between the two halves of the dimer can play an important role It seems likely that such stabilizing effects are larger in salen than in bae complexes

E CONCLUSIONS

A good deal of work has been done on the structural aspects of these Schiff base complexes in order to provide further insight into their physico-chemical behaviour, particular interest being devoted to reversible oxygenation, and to the nature of the chemical bonding in these coordination compounds. Perhaps the most exciting results concern the geometry of the oxygen bridge in the oxygenated adducts[15,33]

However, we think that oxygenated systems need further investigation, particularly to clarify the nature of the bond in the Co–O_2 group present in biological systems[55,56]

With regard to the nature of the coordination bond, it would be interesting to obtain further results on the *trans* and *cis* influence in these and related systems

Finally, in our opinion more extensive structural studies are required on salen and bae derivatives with other metal ions of the transition series, in order to correlate more widely the variability of chemico-physical and structural properties

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