Crystal and Molecular Structures of {*NN*′-[2-(2′-Pyridyl)ethyl]ethylenebis(salicylideneiminato)}-iron(II) and -cobalt(II)–Ethanol (1/1)

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The crystal and molecular structures of the title complexes, [Fe(salpeen)] (1) and [Co(salpeen)]·EtOH (2), have been determined using three-dimensional *X*-ray diffraction data collected on automatic diffractometers. Complex (1) crystallises in the monoclinic space group $P2_1/c$ with the unit-cell parameters a = 10.572(2), b = 11.465(2), c = 16.640(3) Å, β = 90.52(1)°, and Z = 4, and its structure has been refined by conventional least-squares techniques using 1 118 reflections having $I > 3\sigma_I$ to give R 0.056 and R' 0.062. Complex (2) crystallises in the triclinic space group $P\bar{1}$ with the unit-cell parameters a = 15.049(2), b = 15.127(2), c = 10.258(1) Å, α = 90.53(1), β = 93.53(1), γ = 109.81(1)°, and Z = 4, and its structure has been refined using 1 237 reflections having $I > 3\sigma_I$ to give R 0.064 and R' 0.069. The cobalt complex thus has two crystallographically independent molecules in the asymmetric unit, each hydrogen bonded *via* an oxygen atom to an ethanol adduct molecule; there are small but significant differences between the two molecules. The iron and cobalt complexes have a similar distorted trigonal-bipyramidal geometry.

THE structures of five-co-ordinate complexes of iron(II) and cobalt(II) are of some significance with regard to changes in geometry that occur on formation of a dioxygen adduct. Studies of such complexes, containing a dianionic quadridentate ligand capable of assuming an essentially square-planar geometry (such as a porphyrin or Schiff base) or a conjugated amine ligand (such as imidazole or pyridine), are comparatively rare. In their crystal structures, the tetraphenylporphinato-complexes [Fe(tpp)(2Me-im)],[1] [Co(tpp)(1Me-im)],[2] [Co(tpp)(1,2Me$_2$-im)],[3] and [Co(tpp)(3,5Me$_2$-py)] [4,5] are all square pyramidal.† The complex [Co(salen)(py)],[6] which features the more flexible Schiff-base ligand, also exhibits square-pyramidal geometry in the crystalline state, but [Co(3F-saltmen)(1Me-im)] has a distorted trigonal-bipyramidal geometry.[7] The complex [Co(salbn)(py)] crystallises with two crystallographically independent molecules; one has square-pyramidal geometry, the other distorted trigonal-bipyramidal geometry.[8]

In this paper the crystal and molecular structures of the title complexes [Fe(salpeen)] (1) and [Co(salpeen)] (2) are reported and compared. The cobalt complex and its dioxygen adduct have been communicated briefly.[9] The following paper [10] gives the full crystal and molecular structure of the dioxygen adduct and discusses stereochemical changes accompanying oxygenation. The iron(II) complex does not form an easily isolable dioxygen adduct; rapid irreversible oxidation of the type commonly observed for iron(II) complexes [11] is presumed to have occurred.

EXPERIMENTAL

Thin plate-like red crystals of [Fe(salpeen)] (1) and [Co(salpeen)] (2) were both prepared according to ref. 9(*a*). Both complexes are high spin: $\mu_{\text{eff.}}$ = 5.14 for (1) and 4.25 B.M. for (2) at 20 °C.‡ Crystal data and data-collection procedures are summarised in Table 1. The intensity data obtained were corrected for background and Lorentz and polarisation effects. The intensities of three standard reflections well separated in reciprocal space were used to ensure that the relative intensity data for each analysis were correctly scaled.

Throughout this work full-matrix least-squares refinements were based on F_c and the function minimised was $\Delta = \Sigma w(|F_o| - |F_c|)^2$. The weights, w, were taken as $4I/\sigma_I^2$ where σ_I is the standard deviation in the intensity I estimated from counting statistics. $|F_o|$ and $|F_c|$ are the observed and calculated structure-factor amplitudes, respectively. Agreement factors were defined as $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_c| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. The standard error in an observation of unit weight was $[\Delta/(N_O - N_V)]^{\frac{1}{2}}$ where N_O is the number of observations and N_V the number of variable parameters used to describe the structural model. Atomic-scattering factors for non-hydrogen atoms were taken from Cromer and Mann,[12] for hydrogen atoms from Stewart *et al.*[13] The effects of anomalous dispersion for iron and cobalt were included in F_c (ref. 14) using Cromer's values.[15]

[Fe(salpeen)] (1).—The structure was solved by direct methods. Phases were obtained for 428 out of the 464 strongest E values. Notwithstanding a program bug which resulted in the E map being calculated with all the E values having the same magnitude, elucidation of most of the

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† Abbreviations: tpp = *meso*-Tetraphenylporphinate; salen = *NN*′-ethylenebis(salicylideneiminate); 3F-saltmen = *NN*′-tetramethylethylenebis(3-fluorosalicylideneiminate); salpeen = *NN*′-[2-(2′-pyridyl)ethyl]ethylenebis(salicylideneiminate); 1Me-im = 1-methylimidazole; 2Me-im = 2-methylimidazole; 1,2Me$_2$-im = 1,2-dimethylimidazole; 3,5Me$_2$-py = 3,5-dimethylpyridine; py = pyridine; salbn = *NN*′-butane-1,4-diylbis(salicylideneiminate).

‡ Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} Am^2.

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structure was possible. Remaining non-hydrogen atom positions were established using Fourier syntheses, and their positional and thermal parameters refined. Most hydrogen atoms were located in Fourier syntheses and included in the model at their idealised positions with r(C–H) 1.0 Å and temperature factors derived from those of the attached carbon atom, *viz.* $B_H = B_C + 1.0$ Å^2. The hydrogen atoms were not refined and their positions were recalculated after each cycle. Refinement converged satisfactorily (Table 1). The final error in an observation of unit weight was independent of F_0 and $(\sin\theta)/\lambda$ indicating a satisfactory weighting scheme. There was no evidence for secondary extinction among strong low-angle reflections. For data having $I \leqslant 3\sigma_I$ there were no serious or systematic discrepancies between F_0 and F_c with respect to σ_I.

TABLE 1

Crystal data and data collection

	[Fe(salpeen)] (1)	[Co(salpeen)] (2)
Molecular formula	$C_{23}H_{21}FeN_3O_2$	$C_{23}H_{21}CoN_3O_2 \cdot C_2H_6O$
Formula weight	427.3	476.5
Crystal symmetry	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14) [a]	$P\bar{1}$ [b]
a, b, c (Å)	10.572(2), 11.465(2), 16.640(3) [c]	15.049(2), 15.127(2), 10.258(1) [c]
α, β, γ (°)	90, 90.52(1), 90	90.53(1), 93.53(1), 105.81(1)
Z	4	4
D_c, D_m(g cm^{-3})	1.41, 1.40(1) (flotation)	1.41, 1.30(1) (flotation) [d]
Crystal dimensions(mm)	0.18 (max.), 0.06 (min.)	0.33, 0.25, 0.03
μ/cm^{-1}	63.1 (Cu-$K\alpha_1$, λ 1.541 8 Å)	8.31 (Mo-$K\alpha$, λ 0.710 7 Å)
Transmission coefficients	0.70 (max.), 0.55 (min.) [e]	0.98 (max.), 0.79 (min.) [e]
Diffractometer	Syntex $P2_1$ (four-circle)	Hilger and Watts (four-circle)
Temperature (θ_c/°C)	20	23
Monochromatisation	Graphite monochromator	Zr filter
Scan type	θ—2θ symmetric	θ—2θ symmetric
Scan width (°)	*f*	0.72
Scan time (t/s)	*f*	72
Background time (t/s)	*f*	18
$\theta_{max.}$/°, $(\sin\theta)/\lambda$ (Å^{-1})	50.0, 0.50	18.0, 0.43
Number of unique intensities collected	2 401	3 105
Number of intensities with $I > 3\sigma_I$	1 118 [g]	1 237 [g]
p Factor for optimal weighting	0.05 [h]	0.06 [h]
Number of variable parameters	122	129 × 2
Final shift/e.s.d.	0.02	0.10
Final R, R'	0.056, 0.062	0.064, 0.069
Error in observation of unit weight	1.52	1.35

[a] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 1. [b] By structure determination. [c] Cell parameters, crystal orientation, and data collection at 20 °C for (1) and at 23 °C for (2). [d] Loss of adduct occurred. [e] Data for (2) but not (1) were corrected for absorption using DABS, a local version of DATAPH (P. Coppens). [f] Variable: based on a preliminary scan through each reflection. [g] Only data having $I > 3\sigma_I$ used in refinement. [h] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[Co(salpeen)]·EtOH (2).—Space group $P\bar{1}$, with two crystallographically independent molecules in the formula unit, was assumed and subsequent refinement confirmed this choice. A three-dimensional Patterson synthesis yielded co-ordinates for the two cobalt atoms of the asymmetric unit. Successive cycles of least-squares refinements and Fourier syntheses established co-ordinates for the non-hydrogen atoms and for some hydrogen atoms. All the hydrogen atoms in [Co(salpeen)] were included in the model as before. Refinements were conducted in two blocks with each block containing the two cobalt atoms, the two ethanol adduct molecules, and one or other of the two crystallographically independent salpeen ligand systems. Refinements converged satisfactorily (Table 1). The weighting scheme was satisfactory and there was no evidence for secondary extinction.

Table 2 lists the final atomic parameters for both crystal structures. Here and elsewhere the estimated standard deviation in the least significant digits is quoted in parentheses and is conventionally derived from the inverse of the least-squares matrix.

Calculations were carried out at the University of Canterbury, New Zealand using a Burroughs 6718 computer; the data-processing program HILGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens). Numerical absorption corrections were applied using DABS, a modified version of DATAPH (P. Coppens). Structure-factor calculations and least-squares refinements were carried out using program CUCLS and Fourier summations using FOURIER. These are highly modified versions of ORFLS (W. R. Busing, K. O. Martin, and H. A. Levy), and FORDAP (A. Zalkin), respectively. Programs SHNORM and SAP, derived from NRC-4 (S. R. Hall and F. R. Ahmed), were used to calculate normalised structure factors (E values) and derive phases.

Comprehensive tables of structure factors, bond distances, bond angles, non-hydrogen intermolecular contacts (<3.75 Å), and selected least-squares planes and the deviations of atoms therefrom are deposited as Supplementary Publication No. SUP 22173 (22 pp.).* A selection of torsional angles is deposited in the supplementary material of the following paper.

DISCUSSION

The crystal structure of (1) consists of well separated molecules of {*NN'*-[2-(2'-pyridyl)ethyl]ethylenebis(sali-

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* For details see Notices to Authors No.7, *J.C.S. Dalton*, 1977, Index issue.

TABLE 2

Final atomic parameters

	[Fe(salpeen)]				[Co(salpeen)] (A)				[Co(salpeen)] (B)			
	X	*Y*	*Z*	*B*	*X*	*Y*	*Z*	*B*	*X*	*Y*	*Z*	*B*
(*a*) Refined atoms [a]												
M	077 33(14)	242 12(14)	656 21(8)	[b]	180 9(2)	093 4(2)	−007 2(3)	3.93(9)	187 6(2)	−499 3(2)	494 4(3)	3.68(9)
O(1)	−016 8(6)	341 9(5)	581 2(3)	4.0(1)	141 5(9)	087 1(8)	169 1(12)	3.9(3)	146 2(10)	−517 7(9)	669 9(12)	4.2(3)
O(2)	226 9(5)	334 2(5)	685 6(3)	4.0(1)	253 4(9)	010 3(8)	036 6(12)	3.7(3)	258 3(9)	−375 1(8)	530 1(12)	3.5(3)
N(1)	−097 2(7)	177 0(7)	692 6(4)	3.85(17)	071 3(11)	127 5(10)	−073 8(15)	3.2(4)	070 2(12)	−588 6(11)	422 1(16)	4.1(4)
N(2)	132 0(7)	125 8(7)	747 7(4)	4.19(18)	206 2(12)	091 7(11)	−189 1(16)	3.9(4)	213 4(12)	−485 6(12)	306 4(15)	3.9(4)
N(3)	161 1(7)	126 0(7)	570 6(4)	4.19(18)	293 1(11)	215 7(10)	021 7(15)	3.0(4)	296 2(11)	−566 1(11)	518 7(16)	3.9(4)
C(1)	−090 3(10)	090 9(10)	760 6(6)	5.5(3)	067 6(14)	135 0(14)	−218 7(20)	3.9(5)	065 4(15)	−597 7(14)	277 7(21)	4.2(5)
C(2)	038 8(9)	033 7(9)	761 7(6)	4.7(2)	160 2(15)	147 6(15)	−272 5(20)	4.3(6)	159 3(15)	−565 6(15)	225 0(20)	4.1(5)
C(3)	052 4(10)	−065 9(10)	700 7(6)	5.7(3)	213 1(15)	252 9(15)	−267 3(21)	4.7(6)	210 3(15)	−643 8(15)	233 3(21)	5.0(6)
C(4)	033 9(9)	−042 6(9)	611 9(6)	5.2(3)	227 2(17)	306 2(16)	−140 5(24)	6.0(7)	222 3(14)	−690 4(14)	360 9(20)	3.6(5)
C(5)	145 7(9)	007 9(9)	568 7(6)	4.5(2)	304 5(16)	297 8(15)	−049 5(20)	4.2(5)	304 0(15)	−640 0(14)	451.3(19)	3.2(5)
C(6)	229 9(10)	−060 2(9)	526 4(6)	5.2(3)	390 7(20)	367 5(18)	−036 5(25)	7.3(7)	379 7(16)	−674 2(14)	471 5(19)	3.7(5)
C(7)	323 4(11)	−011 4(11)	482 6(7)	6.6(3)	455 9(16)	356 2(15)	−057 3(23)	5.0(6)	449 5(16)	−630 2(16)	559 5(23)	4.7(6)
C(8)	337 2(11)	109 1(11)	482 3(7)	7.0(3)	444 9(15)	279 9(16)	−131 9(20)	4.5(6)	443 1(16)	−557 1(16)	627 9(21)	4.9(6)
C(9)	252 5(11)	172 7(10)	527 7(6)	6.1(3)	360 4(16)	211 7(14)	108 9(20)	4.0(5)	365 5(16)	−525 2(14)	606 2(20)	3.8(5)
C(10)	−209 9(9)	207 6(8)	669 1(6)	4.2(2)	001 5(14)	133 5(12)	−012 4(19)	2.7(5)	001 5(15)	−628 3(14)	483 3(21)	4.0(5)
C(11)	−232 6(8)	292 6(8)	606 8(5)	3.5(2)	−002 6(16)	126 0(14)	126 9(22)	4.4(6)	−001 9(16)	−627 2(15)	623 0(22)	4.2(6)
C(12)	−362 2(9)	310 2(9)	585 3(6)	4.6(2)	−079 7(16)	143 3(14)	−181 9(22)	4.7(6)	−081 8(16)	−681 0(15)	673 7(22)	4.7(6)
C(13)	−392 7(10)	383 3(10)	523 5(6)	5.6(3)	−091 0(16)	138 7(15)	312 1(23)	4.9(6)	−093 8(16)	−687 8(15)	808 6(23)	4.7(6)
C(14)	−302 0(10)	443 5(9)	482 8(6)	5.3(2)	−022 9(17)	117 1(15)	389 8(21)	4.8(6)	−023 5(18)	−632 9(16)	888 9(22)	5.3(6)
C(15)	−174 0(9)	430 8(8)	501 2(6)	4.3(2)	052 6(15)	100 6(14)	347 5(21)	3.9(5)	056 9(15)	−576 7(14)	846 9(21)	4.3(6)
C(16)	−137 7(9)	352 2(8)	565 5(5)	3.6(2)	066 7(15)	105 6(14)	210 8(21)	3.6(5)	070 4(15)	−572 1(14)	711 1(20)	2.9(5)
C(20)	237 8(10)	124 4(9)	786 5(6)	4.5(2)	263 4(14)	057 6(14)	−243 3(19)	3.2(5)	268 0(14)	−421 0(14)	249 1(19)	3.4(5)
C(21)	335 9(9)	209 6(8)	780 9(6)	3.8(2)	319 4(13)	006 4(13)	−173 1(19)	2.7(5)	324 4(14)	−338 1(14)	321 1(21)	3.4(5)
C(22)	447 8(10)	192 9(9)	827 0(6)	5.1(3)	381 3(14)	−029 4(13)	−240 8(19)	3.2(5)	389 3(17)	−277 8(17)	250 2(21)	5.0(6)
C(23)	542 1(10)	273 3(10)	828 9(6)	5.2(2)	433 6(15)	−081 2(15)	−186 5(22)	4.4(6)	444 9(15)	−196 4(16)	305 8(22)	4.7(6)
C(24)	528 2(10)	376 0(10)	787 8(6)	5.4(3)	423 2(15)	−100 0(14)	−056 7(23)	4.7(6)	437 3(16)	−178 2(15)	437 8(23)	5.3(6)
C(25)	420 4(9)	396 7(9)	740 6(6)	4.6(2)	364 0(15)	−069 7(14)	018 1(20)	4.1(6)	375 8(15)	−236 6(15)	510 7(19)	3.6(5)
C(26)	324 0(9)	312 9(9)	733 9(6)	4.0(2)	307 2(14)	−017 3(18)	−039 1(20)	3.5(5)	316 6(14)	−320 9(14)	458 6(20)	3.2(5)
O(S1)					273 7(11)	082 7(11)	374 3(15)	7.6(5)	280 1(10)	−438 7(11)	872 8(14)	6.6(4)
C(S1)					308 7(18)	002 8(18)	365 5(23)	6.2(7)	297 9(16)	−344 8(17)	865 2(22)	5.8(6)
C(S2)					231 8(19)	−083 6(18)	354 8(24)	7.0(7)	216 2(19)	−306 5(18)	851 8(25)	7.8(8)
(*b*) Hydrogen atoms												
H(1A)	−157	030	753	[d]	024	076	−258	[e]	038	−665	245	
H(1B)	−104	133	813		042	187	−246		026	−561	233	
H(2)	054	−000	816		152	127	−370		154	−548	128	
H(3A)	−011	−127	716		183	286	−335		275	−617	205	
H(3B)	140	−098	708		279	259	−294		177	−693	164	
H(4A)	−038	013	606		165	281	−095		224	−755	337	
H(4B)	012	−118	585		231	373	−158		159	−698	403	
H(6)	222	−147	528		390	367	−035		387	−731	421	
H(7)	382	−062	451		514	412	072		509	−650	575	
H(8)	405	148	451		497	275	199		494	−524	700	
H(9)	261	260	528		352	151	167		363	−465	661	
H(10)	−284	170	696		057	140	−068		−058	−664	425	
H(12)	−430	269	615		−129	163	121		−137	−715	607	
H(13)	−484	393	508		−147	150	352		−147	−733	845	
H(14)	−328	498	439		−033	111	488		−036	−630	985	
H(15)	−109	475	471		103	086	415		109	−538	916	
H(20)	253	058	824		271	065	−345		275	−427	149	
H(22)	457	119	859		388	−014	−336		398	−296	155	
H(23)	621	258	860		482	−102	−237		489	−150	247	
H(24)	596	436	791		456	−146	−018		479	−119	481	
H(25)	412	473	711		364	−083	117		375	−219	609	
H(S1A)					353	003	440		336	−320	788	
H(S1B)					347	011	282		335	−312	947	

[a] Fractional co-ordinates are generated by placing 0. prior to the first digit. [b] Anisotropic parameters for Fe: $\beta_{11} = 0.009\,33(16)$, $\beta_{22} = 0.005\,88(13)$, $\beta_{33} = 0.003\,43(6)$, $\beta_{12} = 0.000\,09(17)$, $\beta_{13} = -0.000\,27(7)$, $\beta_{23} = 0.000\,45(10)$, where the form of the anisotropic thermal ellipsoid is $\exp[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. Root-mean-square components of thermal displacement along the principal ellipsoidal axes are 0.193(3), 0.220(2), and 0.233(2) Å. [c] Hydrogen-atom positions were not refined. Hydrogen atom H(1A) is bonded to carbon atom C(1), *etc.* [d] Temperature factor derived from attached carbon atom, $B_H = B_C + 1$. [e] All the hydrogen atoms were given a temperature factor of $B_H = 6.0$.

cylideneiminato)}iron(II). Figure 1 provides a perspective view of complex (1) together with the atom-labelling scheme. The only non-hydrogen intermolecular contacts less than 3.5 Å are: O(2) ··· C(1) 3.40, O(1) ··· C(2) 3.43, C(6) ··· C(11) 3.47, and N(1) ··· C(3) 3.47 Å. The Fe ··· C(3) intermolecular separation is rather close at 3.53 Å. Figure 2 is a stereoscopic view of the contents of the unit cell.

The cobalt crystal structure comprises two crystallographically independent molecules of (2) with each molecule hydrogen bonded to an ethanol molecule [O(S1)–H ··· O(1) 2.82 Å for both molecules A and B]. Figure 3 is a stereoscopic view of the packing of (2) and the ethanol adduct molecule in the unit cell. Closest contacts not involving hydrogen atoms are: C(15) ··· O(S1) 3.39, C(13) ··· C(20) 3.40, C(24) ··· C(24) 3.41, C(15) ··· O(S1′) 3.43, C(8) ··· C(8′) 3.44, O(2) ··· C(S1) 3.44, and O(2′) ··· C(S1′) 3.46 Å.* The relative orientations of the ethanol adduct molecule to the complex are strikingly similar for the two crystallographically independent species. The co-ordination of a pyridyl group (which is linked by an ethyl group to the ethylene

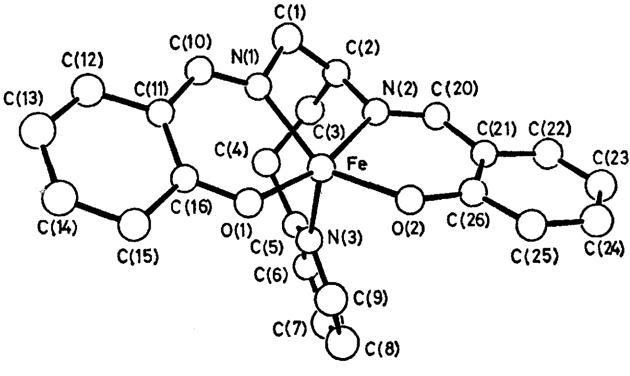

FIGURE 1 Perspective diagram of [Fe(salpeen)], showing the atom-labelling scheme, drawn using ORTEP2 (C. K. Johnson). The ellipsoids enclose 30% probability

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* Here and elsewhere, atoms of molecule B are distinguished from those of A by a single prime.

bridge of the Schiff base) induces deviations of the quadridentate bis(salicylideneiminate) fragment from the square-planar conformation commonly adopted in the four-co-ordinate species such as [Co(salen)],[16] [Co(bzacen)],[17] and [Co(3Bu^t-saltmen)] [18] [bzacen = *NN'*-ethylenebis(benzoylacetoneiminate) and 3Bu^t-saltmen = *NN'*-tetramethylethylenebis(3-t-butylsalicylideneiminate)].

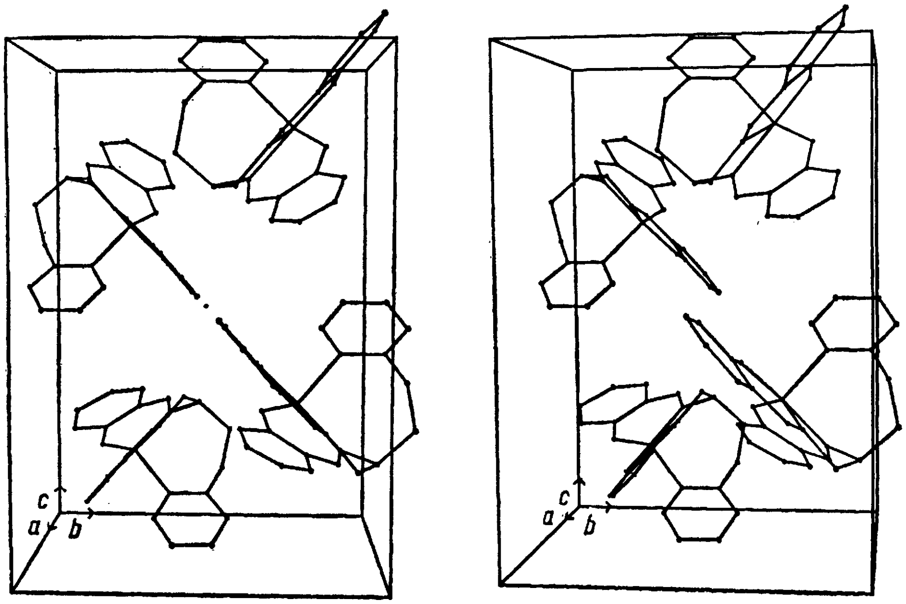

FIGURE 2 Stereoscopic view down the *a* axis of the packing of [Fe(salpeen)] in the unit cell. Perspective view distance, 30 in

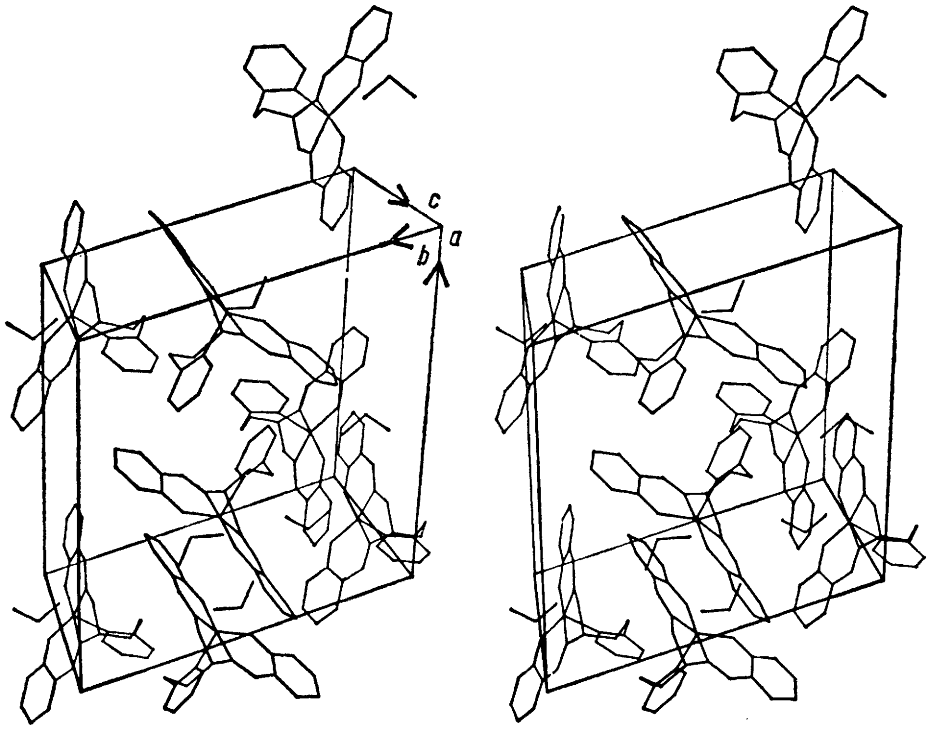

FIGURE 3 Stereoscopic view down the *c*-axis of the packing of [Co(salpeen)] in the unit cell. Perspective view distance, 30 in

In both crystal structures the geometry is distorted trigonal bipyramidal with the O(1)-Fe-N(2) group as the quasi-three-fold axis. The bond angle O(1)-Fe-N(2) is

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[16] W. P. Schaefer and R. W. Marsh, *Acta Cryst.*, 1969, **B25**, 1675.

[17] G. A. Rodley and W. T. Robinson, unpublished structure determination.

[18] R. S. Gall, J. F. Rogers, W. P. Schaefer, and G. G. Cristoph, *J. Amer. Chem. Soc.*, 1976, **98**, 5135.

165.4(3)° [173.5(6) and 172.8(7)°].* In the co-ordination polyhedra, the most notable differences between (1) and (2) involve the M–N(salen) separations and the O(1)–M–O(2) bond angles. The Fe–N(salen) separations are 0.08 Å greater than the Co–N(salen) separations, and the O(1)–Fe–O(2) angle is more than 10° greater for (1) than for (2). This is compensated for by contractions, which are distributed fairly evenly, among the other bond angles involving the metal and the salen ligand donor atoms. Table 3 † lists selected bond distances and angles for the co-ordination polyhedra of (1) and the two independent molecules of (2). Differences in M–O(salen) separations for (1) and (2) are small and the three M–N(py) separations are essentially identical.

TABLE 3

Selected bond distances (Å) and angles (°); the values for the molecules A and B of (2) follow those of (1)

M–O(1)	1.958(6)	O(1)–M–N(1)	87.0(3)	N(2)–M–O(1)	165.4(3)
	1.933(13)		91.8(6)		173.5(6)
	1.939(13)		90.5(6)		172.8(7)
M–O(2)	1.960(6)	O(2)–M–N(2)	86.8(3)	N(1)–M–N(3)	110.0(3)
	1.926(10)		92.5(6)		108.6(6)
	1.909(10)		90.2(6)		110.3(6)
M–N(1)	2.085(7)	N(1)–M–N(2)	78.5(3)	N(2)–M–N(3)	88.6(3)
	1.945(14)		83.8(7)		88.9(6)
	2.004(16)		82.9(7)		88.3(6)
M–N(2)	2.101(8)	O(1)–M–N(2)	104.4(3)	O(1)–M–N(3)	98.6(3)
	1.929(17)		89.6(5)		97.0(5)
	1.992(16)		94.0(5)		96.8(6)
M–N(3)	2.147(8)	N(1)–M–O(2)	146.6(3)	O(2)–M–N(3)	99.4(3)
	2 142(13)		155.5(6)		95.5(6)
	2.147(14)		149.2(6)		99.4(6)
C(1)–C(2)	1.514(12)	N(1)–C(1)–C(2)	109.3(8)	C(2)–C(3)–C(4)	120.1(9)
	1.50(3)		112.5(18)		119.8(18)
	1.50(3)		111.8(18)		121.3(18)
C(2)–C(3)	1.536(13)	N(2)–C(2)–C(1)	107.1(8)	C(3)–C(4)–C(5)	116.1(9)
	1.57(3)		104.7(17)		116.8(20)
	1.58(2)		107.6(17)		115.4(17)
C(3)–C(4)	1.513(13)	N(2)–C(2)–C(3)	111.4(8)		
	1.50(3)		113.4(17)		
	1.52(3)		109.1(17)		
C(4)–C(5)	1.504(12)	C(1)–C(2)–C(3)	113.8(8)		
	1.48(3)		109.1(18)		
	1.51(3)		110.6(18)		

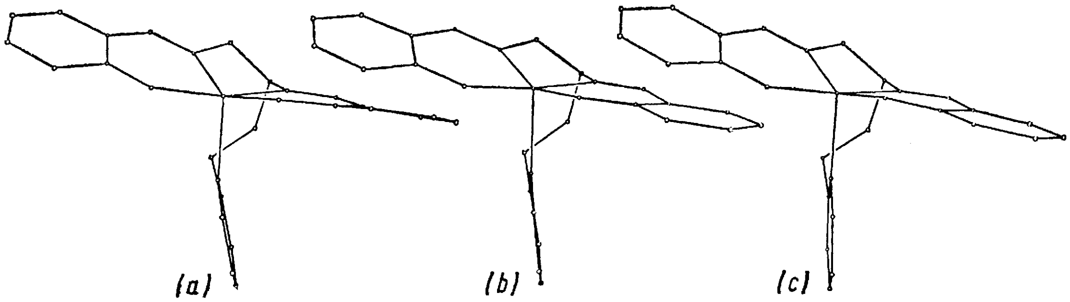

FIGURE 4 Perspective diagrams of [Fe(salpeen)] (*a*) and molecules A(*b*) and B(*c*) of [Co(salpeen)]. The orientation-defining vectors in each case are formed from the same atom combinations

Figure 4 illustrates qualitatively small differences among the three molecules (1), (2A), and (2B). For each case the orientation-defining vectors are formed from the same atom combinations. Quantitatively, the following conformational aspects are noted. The FeO_2N_2 moiety is non-planar. The dihedral angle between planes O(1)–Fe–N(1) and O(2)–Fe–N(2) is 30.7° (25.2 and 30.6°) and the torsional angle N(1)–O(1)–O(2)–N(2) is 16.3(3)° [12.6(5) and 17.2(5)°]. Table 4 lists dihedral angles between a selection of least-squares planes and also the mean absolute displacement of atoms from a particular plane. The two chelate rings, chelate 1 and 2, are not coplanar; neither are the two salicylideneiminate residues sal 1 and 2. The atoms comprising these planes are listed in Table 4.

The Zemann test [19] [$\delta = (\Sigma|XMX_{obs.} - XMX_{theor.}|)/\Sigma|XMX_{theor.}|$] indicates that (1) exhibits greater departures from ideal trigonal-bipyramidal or square-pyramidal symmetries than (2).

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* Immediately following a parameter for (1), the corresponding parameters for molecules A and B of (2), respectively, are quoted in parentheses.

† Bonded distances and angles together with the estimated standard deviations (e.s.d.s) were calculated using CORFFE (a local version of ORFFE; W. R. Busing, K. O. Martin, and H. A. Levy). Torsional angles were calculated using GEOM and unweighted least-squares planes, the dihedral angles between them, and displacements of atoms therefrom using MEAN PLANE (M.E. Pippy and F. R. Ahmed). Diagrams were obtained using ORTEP2, a local version of ORTEP-II (C. K. Johnson, 1970).

[19] J. Zemann, *Z. anorg. Chem.* 1963, **324**, 241.

The co-ordinated pyridyl group has a number of interesting features as a consequence of its attachment to the salen component. First, it is slightly rotated about its normal so that the Fe–N(3)–C(5) angle is 125.5(7)° [126.1(9) and 127.1(9)°] and it is tilted with respect to the Fe–N(3) vector so that the iron atom is 0.516(1) Å [0.293(3) and 0.120(3) Å] out of the pyridyl plane. This alleviates close ethylpyridyl contacts with the salen group. Secondly, the pyridyl plane is orientated with respect to the salen component such that the torsional angle N(1)–Fe–N(3)–C(5) is 31.4(8)° [29(2) and 27(2)°] and N(2)–Fe–N(3)–C(5) is 45.9(8)° [54(1) and 55(2)°]. A non-eclipsing conformation avoids close salen–py contacts. Thirdly, there is evidence of stress in the ethyl group which links the py and salen components. Atom C(4) is displaced by 0.13(1) Å [0.11(2) and 0.11(3) Å] from the pyridyl plane, and there are highly significant departures of the C(2)–C(3)–C(4) and C(3)–C(4)–C(5) bond angles from ideal tetrahedral symmetry (Table 2). Moreover, in all the three molecules the C(2)–C(3) bonds are longer than the other C–C bonds involving sp^3-hybridised carbon atoms, although the differences are of marginal significance. The ethylene bridge adopts the more usual *gauche* conformation [20] with the torsional angle N(1)–C(1)–C(2)–N(2) being 43(1)° [36(2) and 37(2)°].

TABLE 4

Angles (°) between normals to the planes *

	Ph 1	Ph 2	py	sal 1	sal 2	Chelate 1	Chelate 2
I	16.5	14.0	70.1	16.1	11.8	16.3	11.5
N(1), O(1), N(2), O(2)	13.5	7.5	75.9	13.2	7.0	13.7	8.3
$\bar{d}$/Å = 0.213, 0.157, 0.216	15.8	7.3	80.5	15.7	7.7	15.8	9.9
Ph 1		30.1	64.6	1.6	28.0	3.2	28.0
C(11), C(12), C(13), C(14), C(15), C(16)		20.5	69.3	0.8	20.0	1.9	21.7
$\bar{d}$/Å = 0.005, 0.007 0.015		22.0	73.2	0.3	22.5	0.9	25.7
Ph 2			71.3	29.3	2.4	29.2	5.8
C(21), C(22), C(23), C(24), C(25), C(26)			76.6	20.1	0.5	20.3	2.8
$\bar{d}$/Å = 0.018, 0.012, 0.010			79.4	21.8	0.5	21.7	5.4
py				63.3	71.8	61.7	75.6
N(3), C(5), C(6), C(7), C(8), C(9)				68.7	76.6	67.5	79.4
$\bar{d}$/Å = 0.009, 0.018, 0.005				73.2	79.7	72.5	84 5
sal 1					27.3	1.7	27.6
N(1), C(10), C(11) · · · C(16), O(1)					19.6	1.2	21.4
$\bar{d}$/Å = 0.029, 0.023, 0.024					22.3	0.7	25.5
sal 2						27.3	4.1
N(2), C(20), C(21) · · · C(26), O(2)						19.9	2.8
$\bar{d}$/Å = 0.047, 0.011, 0.020						22.2	5.0
Chelate 1							27.8
M, N(1), C(10), C(11), C(16), O(1)							21.8
$\bar{d}$/Å = 0.015, 0.023, 0.026							25.6
Chelate 2							
M, N(2), C(20), C(21), C(26), O(2)							
$\bar{d}$/Å = 0.050, 0.049, 0.057							

* $\bar{d}$ = Mean absolute displacement of atoms (Å) from their least-squares plane in the order (1), (2A), and (2B). The order of the dihedral angles in descending the columns is (1), (2A), and (2B).

For (1) the dispersion (e.s.d. 0.029 Å) of the 12 phenyl C–C bonds about their mean [1.397(29) Å] is statistically significant in comparison with the e.s.d. of an individual bond length (0.011—0.013 Å). For (2) the higher e.s.d.s associated with individual bond lengths mask any possible significance in such dispersion. In addition, differences between chemically equivalent bonds in the two phenyl groups for each molecule are statistically insignificant. The internal consistency is reassuring, but, more importantly, the average bond length for each class closely parallels the well characterised pattern of three long inner bonds and three short outer bonds observed for other related salen derivatives.[20] No significant deviation of the phenyl C–C–C bond angles from their mean value of 120.0° occurs for the three molecules. The phenyl rings (and also the pyridyl ring) are approximately planar; they are also coplanar with their associated chelate rings. Departures of atoms from the least-squares planes for the two nine-atom salicylideneiminate residues are modest.

The two crystallographically independent molecules of (2) provide an excellent demonstration of the effects of crystal packing on molecular stereochemistry. In the immediate co-ordination sphere the most notable difference between the two molecules of (2) is in the Co–N(salen) separations: for molecule A the average separation is 1.94 Å, for molecule B, 2.00 Å. The differences are statistically significant. Other small differences between the two molecules are best appreciated qualitatively by inspection of Figure 4. Small differ-

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[20] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

ences in (*i*) the dihedral angles between the planes O(1),Co,N(1) and O(2),Co,N(2), (*ii*) the torsional angles N(1)-O(1)-O(2)-N(2), and (*iii*) the disposition of the cobalt atoms with respect to the pyridyl plane are noted (see above).

Even more pronounced differences between two crystallographically independent molecules are observed for [Co(salbn)(py)]; one molecule has square-pyramidal geometry, the other is a distorted square pyramid.[8] Thus, in comparing related structures, small differences in stereochemistry about the metal centre may be manifestations of crystal packing and not of intrinsic electronic demands of the metal centre.

The considerable rearrangement of the quinquedentate salpeen ligand that accompanies the co-ordination of dioxygen to [Co(salpeen)] is described in the following paper.

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