Cobalt(III) Compounds of Carbanions and their Reactivity. Part II.[1] Crystal and Molecular Structure of Malononitrilato[propane-1,2-bis(salicylideneiminato)]pyridinecobalt(III)

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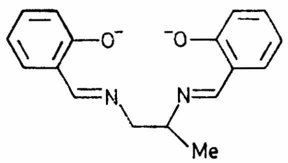
The structure of the title compound has been determined by a three-dimensional *X*-ray structural analysis. Crystals were monoclinic with $a = 9{\cdot}25(3)$, $b = 18{\cdot}14(6)$, $c = 14{\cdot}00(4)$ Å, $\beta = 105{\cdot}3(1)°$, space group $P2_1/c$, and $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques, and was refined anisotropically by block-diagonal least-squares methods, using of 1369 independent reflections, collected on a diffractometer, to a final *R* of 0·061. This analysis confirms the presence of a Co–C bond [2·02(1) Å] in the six-co-ordinate cobalt(III) molecule, and *trans* to it is a long cobalt to pyridine bond [Co–N 2·06(1) Å]. The four donor atoms of the quadridentate ligand are in an essentially planar array with normal bond-lengths [Co–O 1·89(1) and 1·88(1); Co–N 1·91(1) and 1·88(1)]. There is disorder in the 1,2-di-iminopropane chelate ring, which appears to include methyl groups which must be axial substituents on nonsymmetrical chelate rings.

We have recently described [1] the preparation by a novel method of malononitrilato-compounds with cobalt(III) species, such as [Co(salen)(X)(L)] [where salen = (I) for R = H; X = malononitrilato-carbanion and L = unidentate ligand].



(I)

To prove the nature of the reaction products, a three-dimensional *X*-ray crystallographic study of one of them was undertaken. The first compound to give suitable crystals was [Co(salpn)(X)(py)] [where salpn = (I) for R = Me, and py = pyridine].

We have given a preliminary account of this structure,[2] and now report full details of our final refinement.

EXPERIMENTAL

Brown plates, elongated along the *c* axis, were obtained from pyridine.[1] Unit-cell data were obtained from precession photographs.

Crystal Data.—$C_{25}H_{22}CoN_5O_2$, $M = 483{\cdot}4$, Monoclinic, $a = 9{\cdot}25(3)$, $b = 18{\cdot}14(6)$, $c = 14{\cdot}00(4)$ Å, $\beta = 105{\cdot}3(1)°$, $U = 2264{\cdot}5$ Å^3, $D_m = 1{\cdot}42$ (flotation), $Z = 4$, $D_c = 1{\cdot}42$, $F(000) = 1000$. Space group, $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences: $\{h0l\}$, for $l = 2n + 1$, and $\{0k0\}$ for $k = 2n + 1$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) = 7·8 cm^{-1}.

Agreement between the calculated and observed powder diffraction patterns showed that the single crystal was representative of the bulk sample.

Data collection was on a Phillips PAILRED automatic diffractometer. Corrections were applied for Lorentz and polarisation factors, but not for absorption. The total data set, using only reflections with $I/\sigma > 3$, consisted of 1369 independent reflections.

The Patterson function, calculated from this data set, gave the position of the heavy atom (cobalt). From this, after one cycle of least-squares refinement, an observed Fourier synthesis gave the positions of the remaining non-hydrogen atoms except for the methyl carbon atom of the 'pn' chelate ring. Seven cycles of block-diagonal least-squares refinement of the positional and isotropic thermal parameters reduced *R* to 0·098.

A difference Fourier synthesis at this stage showed a peak in the position expected for an equatorial methyl substituent of a gauche pn chelate ring; but refinement of this model, although reducing *R* to 0·090 (5 cycles), gave an unrealistic geometry for this part of the molecule.

A new difference Fourier, with all carbon atoms of this chelate ring omitted, showed quite broad peaks for the methylene carbons (*ca.* 2·5 eÅ^{-3}) and at least three further peaks possibly corresponding to alternative sites for methyl substituents with intensities of 1·3, 0·58, 0·47 eÅ^{-3}. These we label (i), (ii), and (iii), respectively, in the further discussion. The most intense peak (i) corresponded to the methyl group used in the earlier refinement, and (ii) also was in a chemically reasonable position as an equatorial substituent, but (iii) could only correspond to an unusual axial substituent.

Various models for the disorder have been tried. (*a*) This used (i) and (ii) (disordered 70 : 30) as equatorial substituents on the different methylene carbons of the one dimethylene chelate ring, and anisotropic thermal motion for all atoms except the disordered carbons. *R* was reduced to 0·071, but the resulting geometry was unrealistic.

(*b*) A difference Fourier having now clearly indicated disorder at the methylene carbon atoms, (i) and (ii) were attached as equatorial substituents to different gauche conformations of the chelate ring. Refinement using two constrained-geometry, five-atom groups as components of the disorder, the relative populations of which were allowed to vary, reduced *R* to only 0·074, and a difference Fourier showed that (iii) had persisted.

The intensity and position of peak (iii) were not compatible with an interpretation as a hydrogen atom; but it is chemically reasonable [3] to interpret it as an axial methyl group on an unsymmetrical chelate conformation. Molecular geometry calculations confirmed that it could be accommodated here without significant atom overcrowding, provided that several of the atoms of the malononitrilato-moiety occupy positions displaced a little from the observed centres of electron density. The large anisotropic thermal

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[1] Part I, D. Cummins, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, 1973, 414.

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

[3] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1969, **8**, 1168.

parameters for these atoms are consistent with some such disorder.

(*c*) Three constrained, idealised five-atom groups with ' methyls ' (i), (ii), and (iii) attached to separate chelate rings were used now. The populations of (ii) and (iii) were further constrained to be equal, as were the isotropic temperature factors for the nitrogens and the methyl carbons of the groups. This reduced R to 0·070, and the inclusion of calculated fixed positions for all hydrogen atoms (except those of the methyl groups) reduced R to 0·061 (C–H 0·98 Å and isotropic thermal vibrations set at 6·0 Å^2). Populations of the components refined to 0·58, 0·21, and 0·21, respectively, but molecular geometry calculations showed that the atoms of the chelate rings had refined into unlikely conformations, and the nitrogen atom positions of the three component groups were rather different.

At this stage, the groups corresponding to (ii) and (iii) were removed leaving only the major population component for the chelate ring, and difference Fouriers both before and after refinement indicated that (ii) was an artifact.

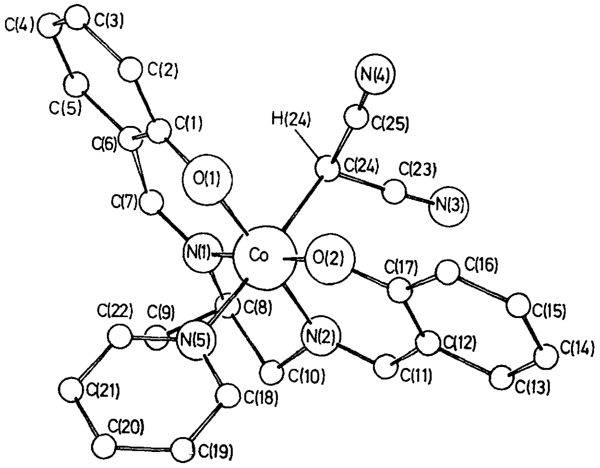

FIGURE 1 The molecular geometry and atom labelling scheme

(*d*) The final model, therefore, used only two eight-atom (N$_2$C$_3$H$_3$) components for the disorder, *i.e.* those involving (i) and (iii). R Was thereby reduced to 0·059, the refined populations were 0·61 and 0·39, and the nitrogen atoms from the different groups had refined into almost identical positions.

Even at this stage, a difference-Fourier synthesis showed further probable components in the disorder, including another peak near the position of H(8) which appears to be another possible axial methyl group on the major conformation of the chelate ring. Clearly we do not yet have a complete model for the disorder, but the data also are not sufficient for a full analysis of it. Since the main chemical interest lies elsewhere, and is not affected by this disorder, we have not pursued the matter further.

Unit weights were used throughout the refinement and no correction was made for anomalous dispersion.

Fractional co-ordinates for atomic positions, with estimated standard deviations, are given in Table 1, together with the calculated positions of the hydrogen atoms (based on C–H 1·08 Å); anisotropic thermal parameters of non-hydrogen atoms are listed in Table 2.

The observed molecular geometry and the atom numbering scheme are given in Figure 1. Hydrogen atoms are given the same numbers as the carbon atoms to which they are bonded, with primes denoting the different hydrogens attached to the same atom. The atoms of the minor disorder component are denoted by adding a 1 to the appropriate atom number of the major component.

TABLE 1

Atom positions with estimated standard deviations in parentheses. The parameters for the high-population group of the disordered pn chelate ring are included in the main Table, and those for the two low-population groups are appended

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Co	0·4722(2)	0·1881(1)	0·1420(1)
O(1)	0·5088(8)	0·1583(4)	0·2757(5)
O(2)	0·3123(8)	0·2442(4)	0·1622(6)
N(1)	0·6320(9)	0·1303(6)	0·1194(7)
N(2)	0·4436(9)	0·2199(6)	0·0104(7)
N(3)	0·1833(17)	0·0875(7)	−0·0751(10)
N(4)	0·1447(19)	0·0948(9)	0·2150(14)
N(5)	0·6127(9)	0·2763(5)	0·1901(6)
C(1)	0·5857(11)	0·1006(5)	0·3144(8)
C(2)	0·5811(12)	0·0788(6)	0·4091(8)
C(3)	0·6640(14)	0·0210(7)	0·4578(9)
C(4)	0·7549(14)	−0·0199(7)	0·4105(10)
C(5)	0·7603(13)	−0·0007(6)	0·3180(9)
C(6)	0·6795(11)	0·0583(6)	0·2675(8)
C(7)	0·7017(12)	0·0791(7)	0·1752(8)
C(8)	0·6417(9)	0·1333(6)	0·0166(8)
C(9)	0·8074(11)	0·1270(12)	0·0143(17)
C(10)	0·5800(12)	0·2093(7)	−0·0232(6)
C(11)	0·3304(12)	0·2585(6)	−0·0406(8)
C(12)	0·2084(11)	0·2824(6)	−0·0051(8)
C(13)	0·0908(13)	0·3184(7)	−0·0731(9)
C(14)	−0·0308(13)	0·3430(6)	−0·0427(10)
C(15)	−0·0365(14)	0·3342(6)	0·0542(10)
C(16)	0·0764(13)	0·2997(7)	0·1198(10)
C(17)	0·2043(12)	0·2729(6)	0·0930(8)
C(18)	0·5625(14)	0·3455(6)	0·1693(10)
C(19)	0·6537(16)	0·4061(6)	0·2056(10)
C(20)	0·7947(14)	0·3952(7)	0·2620(10)
C(21)	0·8447(13)	0·3246(8)	0·2847(10)
C(22)	0·7489(12)	0·2670(6)	0·2484(8)
C(23)	0·2519(14)	0·0941(7)	0·0070(10)
C(24)	0·3362(13)	0·0995(6)	0·1076(9)
C(25)	0·2262(17)	0·0990(8)	0·1672(12)
H(2)	0·511	0·110	0·445
H(3)	0·658	0·006	0·531
H(4)	0·820	−0·066	0·447
H(5)	0·831	−0·032	0·282
H(7)	0·785	0·049	0·150
H(8)	0·581(2)	0·090(1)	−0·027(1)
H(10)	0·553(2)	0·209(1)	−0·103(1)
H(10^1)	0·660(2)	0·252(1)	0·006(1)
H(11)	0·330	0·273	−0·115
H(13)	0·096	0·326	−0·149
H(14)	−0·122	0·370	−0·095
H(15)	−0·132	0·354	0·077
H(16)	0·071	0·292	0·195
H(18)	0·450	0·354	0·123
H(19)	0·615	0·462	0·188
H(20)	0·866	0·442	0·290
H(21)	0·957	0·316	0·331
H(22)	0·787	0·211	0·265
H(24)	0·413	0·054	0·123
N(11)	0·6384(15)	0·1332(9)	0·1207(9)
N(21)	0·4437(15)	0·2186(9)	0·0086(9)
C(81)	0·6908(7)	0·1674(11)	0·0412(12)
C(91)	0·4724(31)	0·1158(16)	−0·1010(10)
C(101)	0·5502(17)	0·1866(10)	−0·0409(4)
H(81)	0·578(27)	0·220(16)	−0·088(10)
H(81′)	0·748(11)	0·212(14)	0·065(17)
H(101)	0·754(15)	0·133(17)	0·016(19)

Atomic scattering factors were taken from ref. 4. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21306 (11 pp., 1 microfiche).†

Table 2

Anisotropic thermal parameters * (× 10^4)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Co	96·0(17)	20·0(4)	40·5(7)	11·4(14)	32·2(18)	16·3(21)
O(1)	138(12)	27(3)	35(5)	11(5)	25(12)	41(9)
O(2)	105(12)	28(3)	68(6)	9(6)	37(13)	17(9)
N(1)	127(15)	41(4)	43(6)	−3(8)	62(16)	57(13)
N(2)	146(16)	32(4)	47(6)	20(7)	60(16)	20(12)
N(3)	406(36)	53(6)	100(11)	−18(13)	−61(31)	−89(23)
N(4)	458(41)	81(8)	231(20)	−95(21)	505(50)	−189(30)
N(5)	101(13)	31(3)	49(6)	−8(7)	49(14)	6(11)
C(1)	99(17)	20(4)	44(7)	15(8)	−30(16)	−26(13)
C(2)	120(18)	26(4)	49(7)	17(9)	−2(18)	19(14)
C(3)	154(20)	38(5)	47(8)	21(10)	−22(19)	−47(16)
C(4)	134(20)	33(5)	66(9)	11(10)	−12(21)	17(15)
C(5)	137(19)	21(4)	70(9)	−2(10)	7(21)	14(14)
C(6)	91(16)	19(4)	57(8)	−14(9)	8(17)	18(12)
C(7)	121(19)	38(5)	56(8)	−7(10)	43(19)	47(15)
C(11)	138(19)	24(4)	47(7)	25(9)	−5(18)	−1(14)
C(12)	95(16)	22(4)	57(8)	18(9)	−39(18)	−13(13)
C(13)	185(21)	24(4)	65(8)	9(11)	−50(20)	17(17)
C(14)	102(19)	27(4)	104(11)	1(11)	−65(23)	7(14)
C(15)	144(21)	32(5)	91(11)	8(11)	7(23)	12(15)
C(16)	118(18)	31(5)	97(11)	34(12)	26(22)	33(15)
C(17)	119(18)	22(4)	57(8)	26(9)	29(19)	11(13)
C(18)	160(21)	21(4)	80(10)	−3(10)	8(23)	23(15)
C(19)	245(27)	23(5)	69(10)	5(11)	18(25)	0(17)
C(20)	168(23)	38(5)	85(11)	−16(12)	23(25)	79(18)
C(21)	119(19)	46(6)	95(11)	10(13)	22(22)	6(18)
C(22)	118(18)	25(4)	57(8)	24(9)	17(19)	−5(14)
C(23)	156(23)	40(6)	90(11)	−8(13)	4(25)	−66(18)
C(24)	139(20)	24(4)	70(9)	−9(10)	63(21)	14(14)
C(25)	278(32)	38(6)	107(13)	−22(14)	145(33)	−25(22)

The atoms N(1), N(11); N(2), N(21); and C(9), C(91); being overlapping or equivalent, their thermal vibrations were correlated in three groups as indicated. The refined isotropic parameter for the carbon atoms was 8·2(6) and the anisotropic parameters for the nitrogen atoms are in the Table. The other carbon atoms were given B values of 5·0, and the hydrogen atoms B values of 6·0, and these were not varied in the refinement.

* The expression for the temperature factors is: $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

RESULTS AND DISCUSSION

The crystals contain, as expected, monomeric units of [Co(salpn)(X)(py)]. Details of the various bond-lengths and angles are given in Table 3, and some least-squares planes within the molecule in Table 4 (we include only the atoms of the highest population component of the disordered pn chelate ring).

The molecule has the same basic structure as a number of closely related Co(salen) species of known structure.[5-8]

Table 3

Bond lengths (Å) and angles (°),* with estimated standard standard deviations in parentheses

(*a*) The co-ordination sphere of the metal

(i) Bond lengths

Co–O(1)	1·891(7)	Co–N(2)	1·882(10)
Co–O(2)	1·877(8)	Co–N(5)	2·060(9)
Co–N(1)	1·906(10)	Co–C(24)	2·019(12)

(ii) Bond angles

O(1)–Co–O(2)	87·0(3)	O(2)–Co–C(24)	90·1(4)
O(1)–Co–N(1)	93·6(4)	N(1)–Co–N(2)	85·5(4)
O(1)–Co–N(2)	177·6(4)	N(1)–Co–N(5)	91·8(4)
O(1)–Co–N(5)	88·1(3)	N(1)–Co–C(24)	89·1(4)
O(1)–Co–C(24)	86·9(4)	N(2)–Co–N(5)	89·7(4)
O(2)–Co–N(1)	178·9(4)	N(2)–Co–C(24)	95·4(4)
O(2)–Co–N(2)	93·9(4)	N(5)–Co–C(24)	174·9(4)
O(2)–Co–N(5)	89·1(3)		

(*b*) The malononitrilato-ligand

(i) Bond lengths

C(23)–C(24)	1·42(2)	C(23)–N(3)	1·16(2)
C(24)–C(25)	1·48(2)	C(25)–N(4)	1·14(2)

(ii) Bond angles

Co–C(24)–C(23)	115·8(9)	C(24)–C(23)–N(3)	178·0(15)
Co–C(24)–C(25)	110·4(9)	C(24)–C(25)–N(4)	176·1(17)
C(23)–C(24)–C(25)	106·2(11)		

(*c*) The pyridine ligand

(i) Bond lengths

N(5)–C(18)	1·34(2)	C(19)–C(20)	1·35(2)
N(5)–C(22)	1·32(1)	C(20)–C(21)	1·37(2)
C(18)–C(19)	1·40(2)	C(21)–C(22)	1·38(2)

(ii) Bond angles

Co–N(5)–C(18)	120·2(8)	C(18)–C(19)–C(20)	119·7(12)
Co–N(5)–C(22)	121·3(7)	C(19)–C(20)–C(21)	119·2(13)
C(18)–N(5)–C(22)	118·2(10)	C(20)–C(21)–C(22)	118·6(12)
N(5)–C(18)–C(19)	121·0(11)	N(5)–C(22)–C(21)	123·2(11)

(*d*) The salpn ligand

(i) Bond angles

O(1)–C(1)	1·30(1)	O(2)–C(17)	1·30(1)
C(1)–C(2)	1·40(2)	C(17)–C(16)	1·42(2)
C(1)–C(6)	1·44(1)	C(17)–C(12)	1·39(2)
C(2)–C(3)	1·37(2)	C(16)–C(15)	1·35(2)
C(3)–C(4)	1·41(2)	C(15)–C(14)	1·37(2)
C(4)–C(5)	1·35(2)	C(14)–C(13)	1·41(2)
C(5)–C(6)	1·39(2)	C(13)–C(12)	1·41(2)
C(6)–C(7)	1·41(2)	C(12)–C(11)	1·42(1)
C(7)–N(1)	1·27(1)	C(11)–N(2)	1·30(1)

(ii) Bond angles

Co–O(1)–C(1)	125·2(6)	Co–O(2)–C(17)	125·7(7)
O(1)–C(1)–C(2)	118·2(9)	O(2)–C(17)–C(16)	118·0(10)
O(1)–C(1)–C(6)	124·6(9)	O(2)–C(17)–C(12)	124·6(10)
C(2)–C(1)–C(6)	117·1(9)	C(12)–C(17)–C(16)	117·3(10)
C(1)–C(2)–C(3)	122·5(10)	C(15)–C(16)–C(17)	121·9(11)
C(2)–C(3)–C(4)	119·5(11)	C(14)–C(15)–C(16)	119·9(12)
C(3)–C(4)–C(5)	119·5(11)	C(13)–C(14)–C(15)	120·8(12)
C(4)–C(5)–C(6)	122·3(11)	C(12)–C(13)–C(14)	119·4(11)
C(5)–C(6)–C(1)	119·1(10)	C(13)–C(12)–C(17)	120·6(10)
C(5)–C(6)–C(7)	118·9(10)	C(11)–C(12)–C(13)	116·8(10)
C(1)–C(6)–C(7)	121·7(10)	C(11)–C(12)–C(17)	122·6(10)
N(1)–C(7)–C(6)	125·7(11)	N(2)–C(11)–C(12)	124·9(10)
C(7)–N(1)–C(8)	118·7(10)	C(10)–N(2)–C(11)	121·9(9)

* Here we refer only to the highest population nitrogen atoms of the disordered salpn moiety. Since the pn chelate ring was refined as a fixed idealised group, details of the geometry within this ring are not included. Relevant bond-lengths and -angles involving the minor component used for the disorder are: Co–N(11) 1·92(1), Co–N(21) 1·90(1), C(7)–N(11) 1·29(2), C(11)–N(21) 1·32(2) Å; C(6)–C(7)–N(11) 126·4(12)°, C(12)–C(11)–N(21) 125·9(11)°, C(7)–N(11)–C(81) 125·7(13)°, C(11)–N(21)–C(101), 121·0(12)°.

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

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The Cobalt(III) *Co-ordination Polyhedron*.—The cobalt and the four donor atoms of the salpn moiety are coplanar within experimental error. Bond distances and angles involving these are unexceptionable.

TABLE 4

Equations of the least-squares planes given in the form $lX + mY + nZ = d$ (where X, Y, and Z are co-ordinates in Å referred to the axes a, b, and c^*). The deviations of the various atoms from these planes are given in square brackets. Angles between some of the planes are listed at the end of the Table

Plane	l	m	n	d
Plane (1): O(1), O(2), N(1), N(2)	−0·5652	−0·7687	−0·2993	−5·3802
[Co 0·012, O(1) −0·026, O(2) 0·026, N(1) 0·026, N(2) −0·026, C(7) 0·266, C(11) 0·128]				
Plane (2): Co, O(1), O(2), N(1), N(2)	−0·5652	−0·7688	−0·2993	−5·3691
[Co 0·000, O(1) −0·037, O(2) 0·015, N(1) 0·015, N(2) −0·037, C(7) 0·255, C(11) 0·117]				
Plane (3): C(1)—(6)	0·6866	0·6136	0·3899	5·6931
[Co −0·213, O(1) 0·052, N(1) 0·097, C(1) 0·005, C(2) −0·009, C(3) 0·006, C(4) 0·000, C(5) −0·004, C(6) 0·002, C(7) 0·123]				
Plane (4): C(12)—(17)	−0·4076	−0·8801	−0·2436	−5·2894
[Co 0·253, O(2) −0·075, N(2) 0·087, C(11) −0·011, C(12) 0·004, C(13) −0·005, C(14) 0·005, C(15) −0·005, C(16) 0·004, C(17) −0·003]				
Plane (5): N(5), C(18)—(22)	0·5804	−0·0175	−0·8142	0·6887
[Co −0·079, N(5) 0·016, C(18) −0·003, C(19) −0·009, C(20) 0·010, C(21) 0·003, C(22) −0·016]				
Plane (6): N(3), N(4), C(23)—(25)	−0·0729	0·9954	−0·0622	1·5083
[Co 1·488, N(3) −0·010, N(4) −0·018, C(23) 0·017, C(24) 0·000, C(25) 0·031]				

Angles between planes (°)

(1)–(3)	167·6	(1)–(5)	94·1
(1)–(4)	11·5	(3)–(4)	156·2
(1)–(6)	134·9		

Similarly, the Co–C distance [2·02(1) Å] is of the same order as that found in related compounds (see ref. 7 for a review), as is the long Co–N distance [2·06(1) Å] to the axial pyridine. There are still not enough known structures of such molecules to justify a detailed assessment of the ground-state *trans* and/or *cis*-effects from such bond-length data, although the bond-lengthening (Co–N of 2·06 Å) *trans* to the carbanion is quite marked.

The Axial Ligands.—The bond lengths in the malononitrilato-group are normal; the angles at C(24) are close to tetrahedral values with C–C–C slightly less than and the mean Co–C–C slightly greater than the idealised value of 109·5°. This is paralleled in the other known related Co^{III} alkyls [6,9,10] and may have a steric origin. The planar C_3N_2 moiety is inclined at 45·1° to the {O(1), O(2), N(1), N(2)} plane (Table 4) showing clearly the tetrahedral nature of atom C(24).

The orientation of the malononitrilate with respect to the rest of the molecule is shown by its projection on the {Co, O(1), O(2), N(1), N(2)} plane (Figure 2).

The plane of the pyridine atoms (Table 4) approximately bisects the angles O(1)–Co–N(1) and O(2)–Co–N(2), an orientation which occurs in many other related molecules.[7,11,12]

The Salpn Ligand.—The bond lengths and angles of such parts of the salpn moiety as are firmly located by the analysis compare favourably with those observed for many related salen compounds.[8] The conformation is oblique-puckered [13,14] (Table 4). Both salicylaldiminates bend away from the larger axial ligand (the pyridine), as [7] in [Co(salen)($\text{CH}_2\text{:CH}$)(py)] and various five-co-ordinate species.[8]

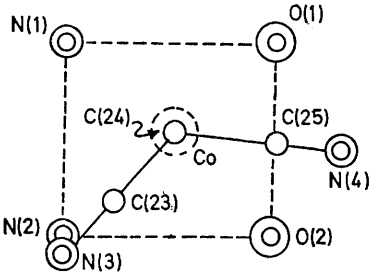

FIGURE 2 Projection of the malononitrilato-group on the {Co, O(1), O(2), N(1), N(2)} plane

There are no intermolecular contacts significantly shorter than the sum of van der Waals radii and no short intramolecular contacts other than those previously mentioned between the malononitrilato-ligand and the lower population conformer of the disordered pn chelate ring.

It is unfortunate that the model used for the disorder of the pn moiety has not been unequivocally established, since there is very little experimental evidence for an axial methyl group in such an octahedral compound. However, as shown by Gollogly and Hawkins,[3] and in this analysis, the conformation does not lead to such gross atom overcrowding that it is unlikely to be found in other future analyses. Curtis and his co-workers [15] have recently reported an example with one of their highly substituted macrocyclic ligands.

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