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PREPARATION AND X-RAY CRYSTAL STRUCTURE OF RACEMIC BIS(ETHYLFUMARATE)BIS(ACETONITRILE)COBALT(0)

G. AGNES, I.W. BASSI *, C. BENEDICENTI, R. INTRITO, M. CALCATERRA and C. SANTINI
Montedison S.p.A., Istituto Ricerche "G. Donegani", Via del Lavoro 4, Novara (Italy)

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Summary

The preparation and properties of some new tetracoordinated cobalt(0) complexes containing nitrile and fumaric ester ligands are described. One of them, $Co(C_2H_5OOCCH{=}CHCOOC_2H_5)_2(CH_3CN)_2$, (Ia), reacts with 1,10-phenanthroline to give new pentacoordinated and hexacoordinated cobalt(0) complexes.

The structure of Ia has been determined from X-ray diffractometer data. The structure was solved by Patterson and Fourier methods and refined by least square techniques to $R = 0.060$ for 2215 independent reflections. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions: a 14.794(18), b 9.448(11), c 10.125(12) Å, α 108.55(9), β 111.42(11), γ 84.95(18)°. The metal is linked to the four carbon atoms of the —CH=CH— groups of the ethyl fumarate residues and to the nitrogen atoms of the two acetonitrile ligands. The coordination of the four ligands around the cobalt atom corresponds to a distorted trigonal pyramid. The four asymmetric carbon atoms of a molecule have the same absolute configuration. *RRRR* and *SSSS* molecules are present in the unit cell.

Introduction

During earlier work we noticed that some cobalt(0) complexes prepared "in situ" were responsible for the dimerization and cyclization of coordinated olefins [1,2] as well as for the catalytic cyclotrimerization of acetylenes [3]. Isolation of pure complexes belonging to this class has now been made possible by following the procedure used by Guerrieri and Salerno [4] for the analogous nickel(0) compounds. The structure of these complexes is of interest

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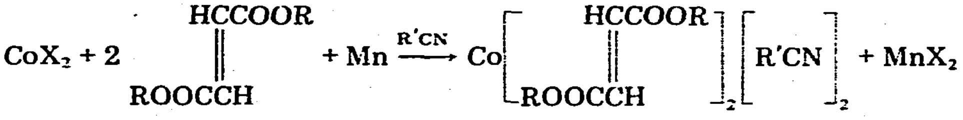
* To whom correspondence should be addressed.

in respect of the coordination around the metal and of the understanding of the role of the metal in catalysis.

The preparation and the X-ray structure of the compound $Co(C_2H_5OOCCH{=}CHCOOC_2H_5)_2(CH_3CN)_2$ (Ia) are reported.

Preparation

Complexes of general formula $Co(ROOCCH{=}CHCOOR)_2(R'CN)_2$ were prepared by reducing an anhydrous cobalt(II) salt dissolved in an organic nitrile (R'CN) in the presence of fumaric esters. Manganese powder proved to be a mild and effective reducing agent for this purpose. The reaction proceeds as follows:



$$CoX_2 + 2\begin{matrix}HCCOOR\\ \|\\ ROOCCH\end{matrix} + Mn \xrightarrow{R'CN} Co\left[\begin{matrix}HCCOOR\\ \|\\ ROOCCH\end{matrix}\right]_2\left[R'CN\right]_2 + MnX_2$$

(Ia—Ic)

(X = Cl, Br, I; Ia: $R = C_2H_5$, $R' = CH_3$; Ib: $R = C_3H_7$, $R' = CH_3$; Ic: $R = C_4H_9$, $R' = C_2H_5$)

Removal of the solvent under vacuum gave an amorphous deep red substance for which a broad IR band at 1620 cm^{-1} suggested coordination between the carboxylic groups of I and the Mn salt [5]. The latter was removed by addition of water; extraction with toluene and precipitation by addition of hexane gave pure I.

Compound Ia is a crystalline, extremely air sensitive deep red compound. Its IR spectrum shows a $\nu(C{=}O)$ stretching band at 1690 cm^{-1} while no $\nu(C{=}C)$ bands due to free fumarate (980 and 1648 cm^{-1}) are present (these bands appear on exposure of the complex to air as the complex decomposes). A sharp, very weak band at 2270 cm^{-1} can be assigned to the coordinated CH_3CN. The shift to higher frequency compared with that of the free ligand ($\nu(C{\equiv}N)$ for CH_3CN = 2250 cm^{-1}) is consistent with coordination through the lone pair of the nitrogen.

Ia is paramagnetic with 3.2 B.M. in the solid state. This high value can be explained by assuming that some of the valence electrons of Co occupy a low-lying orbital of the ligand [6].

Ib and Ic have been isolated as brown red uncrystallizable oils which give good analyses for the proposed formulas. Their IR spectra are almost superimposable on that of Ia. They are extremely air sensitive, very soluble in aromatic hydrocarbons, and almost insoluble in hexane. They react rapidly with protic and halogenated solvents.

Ligand substitution

CO causes complete displacement of the ligands from Ia, Ib and Ic with formation of $Co_2(CO)_8$ in quantitative yield. 1,10-phenanthroline (phen) in contrast brings about stepwise substitution, as follows:

$$Ia + phen \xrightarrow{toluene} \underset{(II)}{Co(C_2H_5OOCCH{=}CHCOOC_2H_5)_2(CH_3CN)(phen)} + CH_3CN$$

$$\mathrm{II + phen \xrightarrow{toluene}}$$

$$\underset{\text{(III)}}{\mathrm{Co(C_2H_5OOCCH{=}CHCOOC_2H_5)(CH_3CN)(phen)_2}} + \mathrm{C_2H_5OOCCH{=}CHCOOC_2H_5}$$

II is a deep red, air sensitive crystalline compound, moderately soluble in aromatic hydrocarbons, very soluble in acetonitrile, and insoluble in hexane. It shows strong IR bands (Nujol mull) at 1685 (ν(C=O)), 1295, 1140, 1042, 840 and 722 cm^{-1}.

III is a greenish black, air-sensitive crystalline compound. It is insoluble in toluene and hexane, and moderately soluble in acetonitrile. The main IR bands (Nujol mull) appear at 1655 (ν(C=O)), 1285, 1187, 1128 and 1048 cm^{-1} and there are two complex groups of bands, the first between 820 and 860 cm^{-1} and the second between 690 and 740 cm^{-1}.

The absence from the IR spectra of II and III, of any band ascribable to the coordinated CH_3—CN is consistent with data for the analogous nickel(0) complexes having this ligand coordinated through the lone pair of the nitrogen [4].

Experimental

All the experiments were carried out under pure nitrogen; solvents were freed of water and oxygen by standard procedures. IR spectra were recorded with a Perkin—Elmer 225 spectrophotometer in Nujol mulls.

Preparation of bis(ethylfumarate)bis(acetonitrile)cobalt(0) (Ia)

11 g (200 mmol) of manganese powder were added to a solution of 6.5 g (50 mmol) of $CoCl_2$ and 17.2 g (100 mmol) of ethylfumarate in 200 ml of CH_3CN. The mixture was stirred for 5 h, during which the colour changed from blue to green and finally to deep red. Unreacted manganese was removed by filtration, and the solvent distilled under vacuum. The residue was shaken with 50 cm^3 of toluene and 5 cm^3 of H_2O. The organic layer was separated, and dried over anhydrous Na_2SO_4. Subsequent addition of 100 ml of n-hexane and storage overnight at —40°C yielded 18.6 g (38.6 mmol) of Ia. The red microcrystalline compound was analytically pure. Found: C, 48.9; H, 6.24; Co, 12. $C_{20}H_{30}CoN_2O_8$ calcd.: C, 49.4; H, 6.18; Co, 12%. Recrystallization from toluene gave good crystals for X-ray study.

Preparation of bis(n-propylfumarate)bis(acetonitrile)cobalt(0) (Ib)

11 g (200 mmol) of manganese powder were added to a stirred solution of 6.5 g (20 mmol) of $CoCl_2$ and 20 g (100 mmol) of n-propylfumarate in 200 ml CH_3CN. Stirring was continued for 5 h. Work-up as above gave a brown red viscous oil. This was redissolved in 10 ml of toluene and precipitated by addition of 50 ml of hexane. Traces of solvent were removed under high vacuum and 16.2 g (30 mmol) of analytically pure Ib were obtained. Found: C, 54; H, 7.1; Co, 9.5. $C_{24}H_{38}CoN_2O_8$ calcd.: C, 53.2; H, 7.04; Co, 9.2%.

Preparation of bis(n-butylfumarate)bis(propionitrile)cobalt(0) (Ic)

From 11 g (200 mmol) of manganese powder, 6.5 g (50 mmol) of $CoCl_2$ and

23 g (100 mmol) of di n-butylfumarate in 200 ml of C_2H_5CN, the above procedure gave 16.2 g (26 mmol) of Ic as a brown-red viscous oil. Found: C, 57.5; H, 7.9; Co, 9.5. $C_{30}H_{50}CoN_2O_8$ calcd.: C, 57.6; H, 8.0; Co, 9.42%.

Preparation of bis(ethylfumarate)acetonitrile-1,10-phenanthrolinecobalt(0) (II)

1.80 g (10 mmol) of 1,10-phenanthroline were added to a solution of 4.85 g (10 mmol) of Ia in 50 ml of toluene. The mixture was stirred for 3 h at room temperature. Cooling at —40°C for 24 h caused separation of 3 g of II as a bright-red powder. Addition of 50 ml of n-hexane to the mother liquor yielded a further sample (2 g) of II. (Overall yield: 80%). Found: C, 57.9; H, 5.7; Co, 9.6. $C_{30}H_{35}CoN_3O_8$ calcd.: C, 57.6; H, 5.6; Co, 9.4%.

Preparation of bis(1,10-phenanthroline)ethylfumarate acetonitrilecobalt(0) (III)

(a) From II. 1.8 g (10 mmol) of 1,10-phenanthroline were added to a stirred suspension of 6.2 g (10 mmol) of II in 30 ml of toluene. Stirring was continued until the solvent became colourless and a fine, black powder precipitated. This was filtered off and redissolved in 20 ml of hot CH_3CN, and the solution was stored at —40°C for 24 h to give 5.1 g of greenish-black glistening crystals (70% yield). Found: C, 64.6; H, 4.95; Co, 9.35. $C_{34}H_{31}CoN_5O_4$ calcd.: C, 64.5; H, 4.9; Co, 9.33%.

(b) From Ia. 3.6 g (20 mmol) of 1,10-phenanthroline were added to a stirred solution of 4.85 g (10 mmol) of Ia in 30 ml of toluene. The procedure described under a gave 5.1 g of III (70% yield).

X-ray analysis

Experimental

Red, needle-like crystals of Ia were examined in Lindemann glass capillary tubes filled with dry nitrogen and flame-sealed. Preliminary space group and unit cell dimensions were obtained from Weissenberg photographs.

A crystal, essentially a parallelepiped, having dimensions ca. 0.40 × 0.30 × 0.50 mm was mounted on a Picker FACS 1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. The orientation matrix and cell dimension were obtained from a least-squares fit of χ, ϕ, ω and 2θ values from 12 independent reflections.

Crystal data

$CoO_8N_2C_{20}H_{30}$, $M = 485.42$, triclinic, a 14.794(18), b 9.448(11), c 10.125(12) Å, α 108.55(9), β 111.42(11), γ 84.95(18)°, U 1248.41 Å^3, $D_m = 1.28$, $Z = 2$, $D_c = 1.29$. Space group $P\bar{1}$. Mo-K_α radiation, λ 0.7107 Å, μ(Mo-K_α) 7.56 cm^{-1}.

Intensity data were collected by use of zirconium-filtered Mo-K_α radiation with $2\theta \leqslant 50°$. The moving-crystal moving-counter technique was used with a 2θ scan rate of 1° min^{-1}, and a scan range of 2.0—2.50° in order to allow for the greater separation of the K_{α_1} and K_{α_2} peaks at increasing 2θ values. Background counts of 10 sec were measured at each end of every 2θ scan. Three standard reflections, measured after every 50 reflections, showed no fluctuation > ±5%

during data collection. 4394 independent reflections were measured of which 2215 were considered observed and had $I \geqslant 2.2\sigma$ $(\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$; where N_s is the total peak count during the time of scanning t_s, and t_b is the time spent in measuring the N_b background counts). An arbitrary intensity of 0.5 of the observable limit was assigned to the non significant reflections. All intensities were corrected for Lorentz and polarization effects. No absorption correction was introduced (μ(Mo-K_α) = 7.56 cm^{-1}).

Determination and refinement of the structure

The structure Ia was solved by the heavy atom method. A three-dimensional Patterson map permitted the location in the unit cell of the cobalt atom. The Fourier map phased on this atom permitted the location of some of the non-hydrogen atoms of the molecule. The location of all the non-hydrogen atoms was achieved by step-wise introduction of the atoms into the structure factor calculations, their coordinates being derived on both Fourier and stereochemical grounds.

The positional and the isotropic thermal parameters of all the non-hydrogen atoms of the molecule, were refined by some cycles of block-diagonal least-squares by use of the program by Immirzi [7]. Atomic scattering factors were calculated from the expression in ref. 8 using values for the parameters given in ref. 9. The weighting scheme of ref. 10 was adopted:

$$\frac{1}{W} = A + B|F_o| + C|F_o|^2$$

where $A = 2\ F_o$ (min), $B = 1.0$ and $C = 2/F_o$ (max). The conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was at this point 0.127 for the 2215 non-zero reflections.

Four block-diagonal cycles of refinement were run, assuming anisotropic thermal parameters for all the non-hydrogen atoms of the molecule. The refinement converged to $R = 0.063$. The final shifts of the atomic parameters were negligible, all being well below the corresponding σ. From a difference Fourier map it was possible to define the coordinates of the four hydrogen atoms of the —HC=CH— groups of both the ethylfumarate residues. The remaining hydrogen atoms were not taken into account because the very high thermal parameters of the carbon atoms to which they are linked. Structure factor calculations performed including also these four hydrogen atoms dropped the R to 0.060 for the 2215 non-zero reflections (assumed B values for these hydrogen atoms 5.0 Å^2).

Table 1 reports the final fractional coordinates and the corresponding estimated standard deviations of the atoms of the molecule Ia. Table 2 lists the anisotropic thermal parameters of the non-hydrogen atoms. A copy of a table of the calculated and observed structure amplitudes can be obtained by application to the authors.

Results and discussion

Views of the molecule Ia are shown in Fig. 1 and 2. Both figures have been obtained by means of the ORTEP computing and drawing programs [11]. The geometrical parameters of the molecule Ia with their estimated standard deviations are reported in Table 3. The cobalt atom is bonded to six atoms: the C(4),

TABLE 1

FINAL FRACTIONAL COORDINATES OF THE INDEPENDENT UNIT OF RACEMIC BIS(ETHYLFUMARATE)BIS(ACETONITRILE)COBALT(0)

The estimated standard deviations (in parentheses) in this and in the other tables, refer to the last significant digit.

Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)
Co	0.21466(6)	0.25668(10)	0.00557(11)	
O(1)	−0.0162(4)	0.0684(6)	−0.2884(7)	
O(2)	0.1138(4)	−0.0749(6)	−0.2838(8)	
O(3)	0.2275(4)	0.4498(5)	−0.2046(6)	
O(4)	0.3373(4)	0.2942(6)	−0.2702(6)	
O(5)	0.2155(4)	0.5114(5)	0.3703(6)	
O(6)	0.2342(4)	0.6158(6)	0.2116(7)	
O(7)	0.4780(4)	0.2577(7)	0.0377(6)	
O(8)	0.4586(3)	0.2014(6)	0.2260(6)	
N(1)	0.2527(4)	0.0501(6)	0.0355(7)	
N(2)	0.0965(3)	0.2788(6)	0.0538(6)	
C(1)	−0.1744(8)	−0.0302(14)	−0.3483(18)	
C(2)	−0.0751(8)	−0.0725(13)	−0.3406(17)	
C(3)	0.0788(5)	0.0484(8)	−0.2668(9)	
C(4)	0.1306(5)	0.1932(7)	−0.2175(8)	
C(5)	0.2300(5)	0.1984(7)	−0.1983(9)	
C(6)	0.2633(5)	0.3269(8)	−0.2221(8)	
C(7)	0.3789(8)	0.4205(11)	−0.2857(13)	
C(8)	0.4493(7)	0.3535(13)	−0.3647(13)	
C(9)	0.0955(8)	0.5828(13)	0.4762(13)	
C(10)	0.1550(8)	0.6370(10)	0.4133(13)	
C(11)	0.2492(5)	0.5137(7)	0.2656(8)	
C(12)	0.2998(4)	0.3759(7)	0.2207(7)	
C(13)	0.3487(4)	0.3649(7)	0.1205(8)	
C(14)	0.4330(5)	0.2689(8)	0.1244(8)	
C(15)	0.5450(6)	0.1078(11)	0.2373(11)	
C(16)	0.5778(10)	0.0863(17)	0.3817(15)	
C(17)	0.2842(4)	−0.0639(7)	0.0380(9)	
C(18)	0.3247(6)	−0.2114(9)	0.0388(12)	
C(19)	0.0233(5)	0.2961(8)	0.0656(8)	
C(20)	−0.0728(5)	0.3135(11)	0.0834(11)	
H(4)	0.091	0.282	−0.211	5.0
H(5)	0.263	0.108	−0.217	5.0
H(12)	0.311	0.308	0.289	5.0
H(13)	0.345	0.441	0.061	5.0

C(5), C(12) and C(13) carbon atoms of the —CH=CH— groups of the ethylfumarate residues, and the N(1) and N(2) nitrogen atoms of the two acetonitrile groups. The average value of the Co—C bond lengths is 2.060(9) Å. This value is in accord with those reported for *trans*-di-μ-carbonylbis(π-2,3-*cis*-dimethylbutadiene carbonylcobalt) [12] (av. 2.084(4) Å), and for $CoC_{12}H_{19}$ [13] (av. 2.09(2) Å).

The atoms N(2), C(4), C(5), C(12) and C(13) are roughly coplanar (r.m.s. distance 0.129 Å). The distance of the cobalt atom from this plane is 0.257 Å and that of the four hydrogen atoms of —CH=CH— ligands about 1.0 Å. Of these, H(5) and H(12) are located over the plane, H(4) and H(13) underneath. The average distance of these hydrogen atoms from the cobalt atom is about 2.4 Å. The Co—N distances are significantly different: Co—N(1) 2.067(7),

TABLE 2

ANISOTROPIC THERMAL PARAMETERS (Å^2) FOR THE NON-HYDROGEN ATOMS OF THE INDEPENDENT UNIT OF I

The temperature factor is in the form: $T_j = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	2.84(03)	3.10(03)	4.35(04)	0.51(02)	1.64(02)	1.28(03)
O(1)	4.74(26)	5.86(29)	8.92(39)	−0.52(22)	1.65(26)	1.79(27)
O(2)	6.20(32)	4.70(27)	1.00(44)	0.12(24)	1.59(30)	1.01(28)
O(3)	6.88(31)	4.93(25)	7.45(34)	1.37(22)	3.72(26)	2.74(24)
O(4)	6.07(28)	5.45(27)	7.27(32)	0.43(22)	3.79(25)	1.85(24)
O(5)	6.92(30)	5.37(27)	7.23(32)	2.27(23)	4.41(26)	2.10(24)
O(6)	6.87(31)	4.82(25)	8.41(37)	1.59(23)	3.96(28)	2.47(25)
O(7)	5.08(27)	9.37(39)	6.97(33)	1.27(26)	3.33(25)	2.88(29)
O(8)	4.41(24)	6.86(30)	6.65(31)	2.20(22)	2.16(22)	2.62(25)
N(1)	4.50(27)	4.31(27)	6.58(35)	0.89(22)	2.41(25)	2.67(26)
N(2)	3.84(24)	4.61(27)	4.73(29)	0.46(21)	2.20(21)	1.56(22)
C(1)	6.45(59)	9.07(73)	16.81(120)	−1.29(53)	4.58(69)	1.98(74)
C(2)	6.87(61)	8.04(67)	15.57(113)	−2.79(52)	1.53(65)	2.17(68)
C(3)	4.87(37)	4.75(36)	5.80(42)	0.71(29)	1.69(31)	1.33(31)
C(4)	4.66(33)	3.95(31)	4.63(35)	−0.26(25)	1.56(27)	1.14(27)
C(5)	4.74(34)	3.89(31)	6.32(42)	0.64(26)	2.70(31)	1.71(29)
C(6)	4.84(34)	4.66(33)	4.74(35)	0.82(27)	2.41(28)	1.77(28)
C(7)	8.95(63)	7.39(55)	10.71(74)	−0.92(47)	6.06(58)	3.24(52)
C(8)	6.85(54)	10.10(71)	9.38(69)	−0.74(50)	4.15(51)	2.50(56)
C(9)	9.68(71)	8.60(65)	9.90(75)	1.76(54)	6.19(62)	2.00(55)
C(10)	9.54(64)	5.63(45)	11.14(74)	2.96(44)	7.29(60)	2.57(47)
C(11)	3.97(30)	4.20(31)	5.56(38)	0.67(25)	1.86(28)	1.68(28)
C(12)	3.76(28)	3.84(29)	4.02(31)	0.70(22)	1.57(24)	1.44(24)
C(13)	3.13(27)	4.37(32)	5.29(37)	0.07(23)	1.46(25)	0.41(27)
C(14)	3.43(30)	5.80(39)	5.61(40)	0.17(27)	1.66(28)	1.02(32)
C(15)	5.64(44)	8.86(59)	7.77(56)	4.28(43)	2.68(41)	2.94(47)
C(16)	12.28(96)	13.88(104)	10.07(84)	7.63(84)	4.35(74)	5.38(78)
C(17)	3.61(29)	4.37(32)	6.69(42)	0.28(24)	2.36(29)	2.35(30)
C(18)	6.15(43)	4.78(37)	11.07(67)	1.79(32)	4.95(46)	3.82(42)
C(19)	3.80(30)	5.36(36)	5.31(38)	0.38(26)	2.17(28)	1.81(30)
C(20)	3.98(36)	9.26(60)	7.98(57)	1.12(37)	3.12(37)	2.14(47)

Co—N(2) 1.957(6) Å; the shortest value is in good agreement with the values quoted in the literature [14]. A nearly tetrahedral symmetry is known for some cobalt zero complexes [15,16], but in the case of Ia the coordination polyhedron is better approximated by a trigonal pyramid. Let us assume that the Co—C bonds may be directed along a straight line joining the Co atom and the mid point of the two —CH=CH— groups. The average value of the Co—ligand distance is about 2.0 Å (the mid points of the —CH=CH— groups and the two nitrogen atoms have been taken into account). Accordingly, if the cobalt atom were in the centre of a tetrahedron, its distances from the four planes defining the tetrahedron itself must be 0.66 Å, while, as said above, the found distance is only 0.257 Å. The atoms N(2), C(4), C(5), C(12) and C(13), as seen before, are nearly coplanar and the angles N(2)—Co—mid-point and mid-point—Co—mid-point are 109.6, 112.1 and 133.0°, respectively. These values are very near to a trigonal symmetry in the plane (note that the cobalt atom is out of the plane defined by the involved atoms), and nearly correspond to the values we have

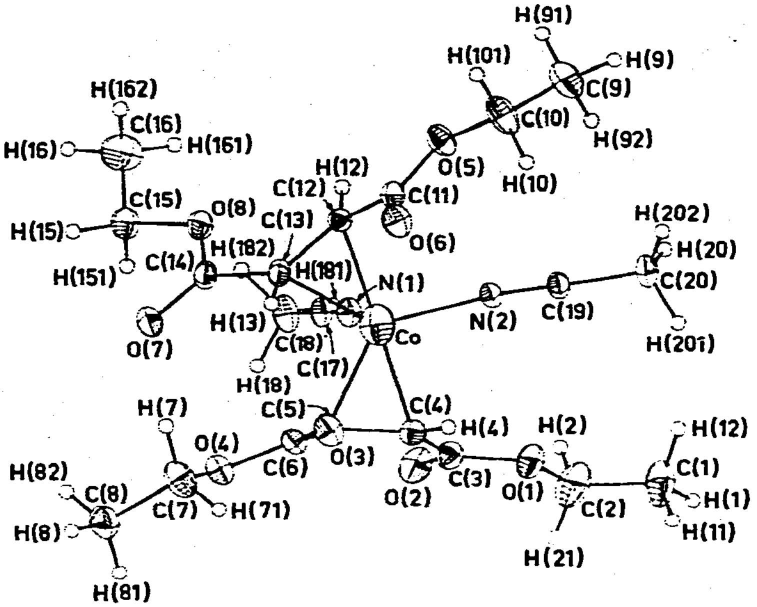


Fig. 1. View of the racemic bis(ethylfumarate)bis(acetonitrile)cobalt(0) molecule indicating the atom labelling scheme, and the 30% probability thermal ellipsoids.

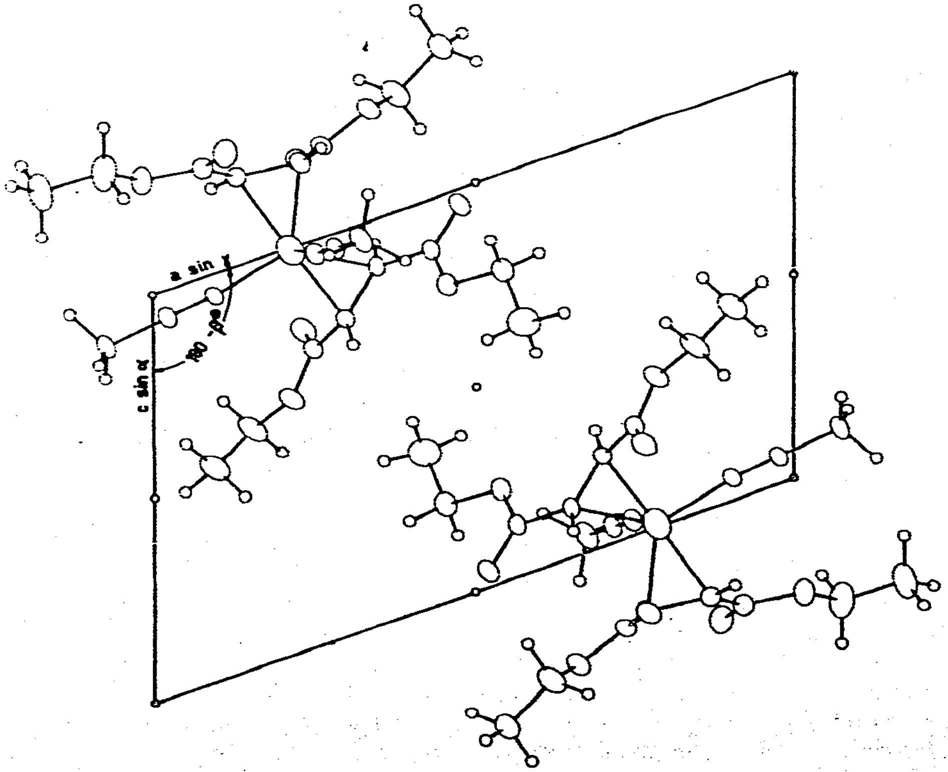
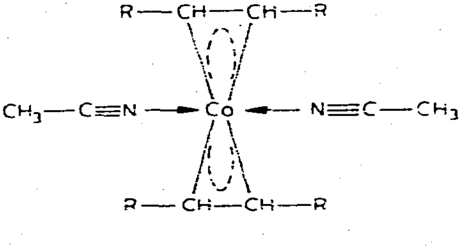


Fig. 2. Packing arrangement of the racemic bis(ethylfumarate)bis(acetonitrile)cobalt(0) molecules viewed down the b-axis.

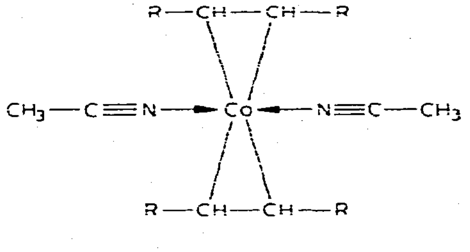
found for racemic bis(ethylfumarate)(acetonitrile)nickel(0) [17]. For (—)-tetracarbonyl(fumaric acid)iron(0) [18], which shows a bipyramidal trigonal coordination, the angles among the atoms in the basal plane, for the A, B and C types of molecules present in the unit cell, are (A) 126.9, 125.5, 107.5°; (B) 122.4, 121.1, 116.6°; (C) 125.4, 125.3, 109.2°, respectively. For racemic tetracarbonyl(fumaric acid)iron(0) [19], having the same coordination polyhedron of the optically active compound mentioned above, the observed angles are 124.2, 122.2, 113.7°.

In the case of Ia the average value of the N(1)—Co—N(2) and N(1)—Co—C angles is 97.0°, and the observed angles indicate that the N(1) atom is nearly perpendicular to the plane defined by the other atoms bonded to the metal. All these geometric considerations indicate trigonal pyramidal coordination around the metal. Compound Ia is paramagnetic, and this is in line with the fact that there is an unpaired electron on the metal.

In Ia the bonding situation around the metal may be represented by two limiting schemes:



(A)



(B)

In the limiting structure A the carbon atoms maintain sp^2 hybridization and their bonding to the cobalt atom is via the delocalised π electrons. In the limiting structure B the carbon atoms present sp^3 hybridization and are bonded to the cobalt via σ electrons.

In the two ethylfumarate chains, the bond lengths and the valence angles are in agreement with the values in the literature [17,18,19]. The succession of the torsion angles on the C(1)····C(8) chain is such as to give an almost perfect planar zig-zag formation. The two oxygen side atoms, O(2) and O(3) are nearly in eclipsed conformation in respect of the chain atoms three bonds apart. In the C(9)····C(16) chain the torsion angles are almost *trans* (180°) up to the C(13)—C(14) bond. The chain oxygen atom O(8), is in eclipsed conformation, while the O(7) side oxygen atom is in *trans* position with respect to C(12). Then the chain proceeds with torsion angles nearly *trans*. The eclipsed conformation assumed by the chain on the C(13)—C(14) bond is almost isoenergetic with the *trans* one; similar eclipsed conformations have been found in the case of deca-*trans*-3-*trans*-7-diene-1,10-dioic acid [20]. The conformation of the chain C(9)····C(16) may be determined by packing requirements. The values of the torsion angles at the double bonds of the R—CH=CH—R groups are interesting in both the ethylfumarate molecules viz. 151° for the C(3)—C(4)—C(5)—C(6) sequence and 152° for the C(11)—C(12)—C(13)—C(14) sequence. In free fumaric acid this angle is exactly 180° [21]. Deviations of these torsion angles from

(continued on p. 412)

TABLE 3

MOST SIGNIFICANT INTRAMOLECULAR BOND LENGTHS AND ANGLES IN RACEMIC BIS(ETHYLFUMARATE)BIS(ACETONITRILE)COBALT(0)

Bond lengths (Å)		Bond angles (Degrees)		Torsion angles (Degrees)		Most relevant intramolecular distances between non-bonded atoms (Å)	
Co—N(1)	2,067(7)	Co—C(4)—C(5)	69,6(5)	C(1)—C(2)—O(1)—C(3)	176	N(2)···C(10)	3,98
Co—N(2)	1,957(6)	Co—C(5)—C(4)	70,0(5)	C(2)—O(1)—C(3)—O(2)	−2	N(2)···O(1)	3,28
Co—C(4)	2,056(10)	Co—C(12)—C(13)	69,3(4)	C(2)—O(1)—C(3)—C(4)	179	N(2)···O(5)	3,21
Co—C(5)	2,051(10)	Co—C(13)—C(12)	70,4(4)	O(1)—C(3)—C(4)—C(5)	185	N(2)···O(6)	3,52
Co—C(12)	2,073(8)	Co—C(13)—C(14)	115,6(4)	O(2)—C(3)—C(4)—C(5)	6	C(19)···O(1)	3,41
Co—C(13)	2,059(8)	Co—C(12)—C(11)	107,2(4)	C(3)—C(4)—C(5)—C(6)	151	C(19)···O(5)	3,52
		Co—C(4)—C(3)	112,4(4)	C(4)—C(5)—C(6)—O(4)	209	C(19)···C(9)	3,98
C(1)—C(2)	1,46(2)	Co—C(5)—C(6)	111,2(4)	C(4)—C(5)—C(6)—O(3)	27	C(19)···C(10)	3,93
C(2)—O(1)	1,49(1)	C(4)—Co—C(5)	40,4(7)	C(5)—C(6)—O(4)—C(7)	184	C(20)···C(9)	3,99
O(1)—C(3)	1,35(1)	C(12)—Co—C(13)	40,2(6)	O(3)—C(6)—O(4)—C(7)	6	C(19)···C(11)	3,62
O(2)—C(3)	1,22(1)	N(2)—Co—C(4)	89,4(2)	C(6)—O(4)—C(7)—C(8)	189	C(19)···C(12)	3,86
C(3)—C(4)	1,48(1)	N(2)—Co—C(5)	129,7(3)			C(19)···C(3)	3,76
C(4)—C(5)	1,42(1)	N(2)—Co—C(12)	92,9(2)	C(9)—C(10)—O(5)—C(11)	157	C(19)···C(4)	3,60
C(5)—C(6)	1,47(1)	N(2)—Co—C(13)	131,1(2)	C(10)—O(5)—C(11)—O(6)	3	N(1)···O(2)	3,04
O(3)—C(6)	1,22(1)	N(1)—Co—N(2)	97,9(1)	C(10)—O(5)—C(11)—C(12)	186	N(1)···O(8)	3,12
C(6)—O(4)	1,33(1)	N(1)—Co—C(4)	100,5(2)	O(5)—C(11)—C(12)—C(13)	186	C(17)···O(2)	3,29
O(4)—C(7)	1,47(1)	N(1)—Co—C(5)	93,3(2)	O(6)—C(11)—C(12)—C(13)	10	C(17)···O(8)	3,33
C(7)—C(8)	1,51(2)	N(1)—Co—C(12)	94,4(2)	C(11)—C(12)—C(13)—C(14)	152	C(17)···C(3)	3,81
C(4)—H(4)	0,97	N(1)—Co—C(13)	98,8(2)	C(12)—C(13)—C(14)—O(8)	−2	C(17)···C(14)	3,68
C(5)—H(5)	0,95	C(4)—Co—C(12)	164,4(4)	C(12)—C(13)—C(14)—O(7)	180	C(17)···C(15)	3,86
		C(4)—Co—C(13)	131,5(3)	C(13)—C(14)—O(8)—C(15)	182	C(17)···C(5)	3,81
C(9)—C(10)	1,46(2)	C(5)—Co—C(12)	134,5(3)	O(7)—C(14)—O(8)—C(15)	0	C(6)···C(14)	3,67
C(10)—O(5)	1,47(1)	C(5)—Co—C(13)	94,3(2)	C(14)—O(8)—C(15)—C(16)	161	C(17)···C(12)	3,96
O(5)—C(11)	1,33(1)					C(17)···C(13)	3,99
O(6)—C(11)	1,22(1)	C(1)—C(2)—O(1)	107,7(5)	N(2)—Co—C(4)—C(3)	−67	O(3)···O(6)	3,97
C(11)—C(12)	1,47(1)	C(2)—O(1)—C(3)	114,7(4)	N(2)—Co—C(4)—C(5)	178	O(4)···O(7)	3,16
C(12)—C(13)	1,42(1)	O(1)—C(3)—O(2)	122,2(4)	N(2)—Co—C(5)—C(4)	−3	O(4)···C(13)	3,74
C(13)—C(14)	1,47(1)	O(1)—C(3)—C(4)	110,5(3)	N(2)—Co—C(5)—C(6)	71	O(4)···C(14)	3,80
O(7)—C(14)	1,25(1)	O(2)—C(3)—C(4)	127,3(3)			O(7)···C(5)	3,55
C(14)—O(8)	1,31(1)	C(3)—C(4)—C(5)	120,3(4)	N(2)—Co—C(12)—C(11)	−48	O(7)···C(6)	3,47
O(8)—C(15)	1,48(1)	C(4)—C(5)—C(6)	116,2(3)	N(2)—Co—C(12)—C(13)	197	O(7)···C(7)	3,81
C(15)—C(16)	1,43(2)	C(5)—C(6)—O(3)	125,7(3)	N(2)—Co—C(13)—C(12)	22		
C(12)—H(12)	1,05	C(5)—C(6)—O(4)	112,0(3)	N(2)—Co—C(13)—C(14)	136		

C(13)—H(13)	1,07	O(3)—C(6)—O(4)	122,3(3)		
		C(6)—O(4)—C(7)	115,0(4)	N(1)—Co—C(4)—C(3)	31
N(1)—C(17)	1,14(1)	O(4)—C(7)—C(8)	105,7(4)	N(1)—Co—C(4)—C(5)	−84
C(17)—C(18)	1,47(1)			N(1)—Co—C(5)—C(4)	79
				N(1)—Co—C(13)—C(12)	−87
N(2)—C(19)	1,13(1)	C(9)—C(10)—O(5)	105,8(4)	N(1)—Co—C(12)—C(13)	82
C(19)—C(20)	1,49(1)	C(10)—O(5)—C(11)	116,0(4)	N(1)—Co—C(13)—C(14)	28
		O(5)—C(11)—O(6)	122,7(4)		
		O(6)—C(11)—C(12)	126,2(3)	H(4)—C(4)—C(5)—H(5)	187
		O(5)—C(11)—C(12)	111,1(3)	H(12)—C(12)—C(13)—H(13)	188
		C(11)—C(12)—C(13)	118,9(3)		
		C(12)—C(13)—C(14)	120,1(4)		
		C(13)—C(14)—O(8)	115,0(3)		
		C(13)—C(14)—O(7)	121,7(3)		
		O(7)—C(14)—O(8)	123,3(4)		
		C(14)—O(8)—C(15)	117,0(4)		
		O(8)—C(15)—C(16)	107,0(6)		
		Co—N(1)—C(17)	167,8(23)		
		N(1)—C(17)—C(18)	179,0(188)		
		Co—N(2)—C(19)	171,4(32)		
		N(2)—C(19)—C(20)	177,7(72)		
		C(3)—C(4)—H(4)	117		
		C(5)—C(4)—H(4)	122		
		Co—C(4)—H(4)	95		
		C(4)—C(5)—H(5)	118		
		C(6)—C(5)—H(5)	118		
		Co—C(5)—H(5)	111		
		C(11)—C(12)—H(12)	114		
		C(13)—C(12)—H(12)	125		
		Co—C(12)—H(12)	108		
		C(12)—C(13)—H(13)	126		
		C(14)—C(13)—H(13)	111		
		Co—C(13)—H(13)	101		

180°, similar to those found in Ia, are known for many analogous complexes and are attributed to achievement of better intramolecular distances [17—19]. Both the acetonitrile ligands have their atoms almost on a straight line, while the angles Co—N(2)—C(19) and Co—N(1)—C(17) are 171.4 and 167.8°. The Co—N distances are significantly different from each other, (Co—N(1) 2.067(7) Å; Co—N(2) 1.957(6) Å), but while N(1) is at the apex of the trigonal pyramid, N(2) lies in the basal plane. This may be connected with the observation of a lengthening of the apical bonds compared with the bonds of the basal plane of a pyramid [22,23]. The N(1)—C(17) and N(2)—C(19) bond lengths are almost identical, 1.131(1) Å, and this distance indicates a triple bond character for both bonds.

All the intramolecular distances are good (see Table 3). The packing consists in the arrangement of up and down enantiomorphous molecules about the inversion centres of the unit cell. A survey of the intermolecular Van der Waals separations reveals that the shortest values for C····O, N····C and C····C distances are 3.24, 3.80 and 3.58 Å, respectively.

The asymmetric centres of the ethylfumarate ligands have the same absolute configurations. On the basis of the coordinates in Table 1, the sequence rule proposed by Cahn, Ingold and Prelog [24] would lead to designation of the four asymmetric carbon atoms as *RRRR*. A single molecule of Ia, therefore, must be optically active. The crystals of Ia cannot have optical activity as they belong to a centrosymmetric space group. Analogous situations have been found in similar complexes [17—19].

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