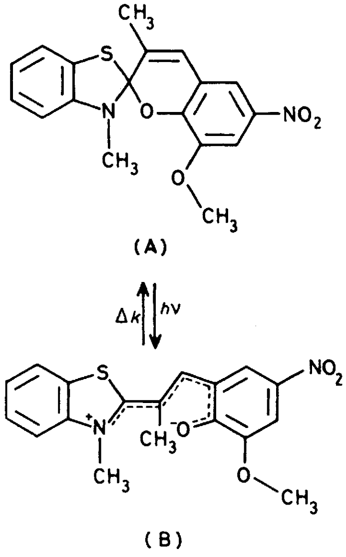
Crystal and Molecular Structure of $CoCl_2(L)(1/2$ Acetone) where L is = [8-Methoxy-3-methyl-6-nitro-2*H*-1-benzopyran-2-spiro-2′-(3-methylbenzothiazoline)]

Erika Miler-Srenger * **and Robert Guglielmetti**
U.A. 473 et Laboratoire de Chimie Structurale Biomoléculaire, U. F. R. Santé, Médecine et Biologie Humaine, Université Paris XIII, 74 rue Marcel Cachin, 93012 Bobigny, France

The molecular structure of the title compound has been determined by *X*-ray analysis. The structure was solved by the multisolution technique and the atomic parameters refined by full-matrix, least-squares calculations, to an *R* value of 0.09 for 2 544 observed reflexions. There are two molecules in the asymmetric unit: one in the form of dimer (**A**) and the other in the form of monomeride (**B**). In both molecules the co-ordination sphere of the cobalt atom is composed of oxygen and chlorine atoms. The geometry of the co-ordination polyhedra is determined from the mean angular and dihedral angle deviation from idealized trigonal bipyramidal and tetragonal pyramidal models. It can be described as a more [in (**A**)] or less [in (**B**)] distorted trigonal bipyramid. The geometry of the ligand could be associated with that of the hypothetical intermediate of the spiropyran $\rightleftarrows$ merocyanine photoconversion process. In the crystal lattice, molecular stacks of monomeric (along *b*) and dimeric complexes (along *a*) are formed and cross-linked through short van der Waals contacts. I.r. and solid-state reflectance spectra are given.

Colourless photochromic spiropyran compounds (**A**) are transformed by the action of u.v. light into strongly coloured photomerocyanines (**B**). The reaction has been described as a stepwise process, though intermediates were never isolated. The first stage of the photochemical conversion should be opening of the pyran ring through C(22′)–O(1) bond rupture. In the high-energy isomer so formed the pyran oxygen is still close to the spiran carbon atom, and steric repulsions are balanced by electrostatic attractions between the negatively charged pyran oxygen and the positively charged heterocyclic ring. The pyran oxygen and the spiran carbon atom are on the same side of the double bond in the methine chain. This sterically unstable isomer undergoes a series of rearrangements involving the methine chain. Coplanarity is attained through rotation of the two parts of the molecule in relation to each other. Finally an equilibrium mixture of different stereoisomers is established. The reaction is reversible: after the rearrangement in the methine chain, and the relative rotation of the two parts of the molecule, the spiropyran is restored. In order to control the spiropyran $\rightleftarrows$ merocyanine photoconversion process first-row transition metal and zinc halides have been added to the starting and end products of the photochemical reaction. Attempts to establish, without ambiguity, the molecular structure of the different spiropyranmetal complexes through electronic and i.r. spectral measurements failed. Hence an *X*-ray crystal structure analysis of the title compound, the sole complex to form monocrystals, has been undertaken.



(A)

(B)

Experimental

Synthesis.—Anhydrous cobalt(II) chloride (1 mmol) was dissolved in anhydrous acetone and added to an anhydrous acetone solution of the appropriate benzothiazolinespiropyran (1 mmol). The mixture was refluxed for a few minutes. Slow cooling of the solution in the dark yielded small green monocrystals of the cobalt complex [Found: Co, 11.4; Cl, 13.8; C, 45.2; H, 3.6; N, 5.4; S, 6.2. Calc. for $C_{18}H_{16}Cl_2CoN_2O_4S{\cdot}0.5(C_3H_6O)$: Co, 11.4; Cl, 13.8; C, 45.5; H, 3.7; N, 5.4; S, 6.2%].

Crystal data. $M_W = 515.3$, triclinic, space group $P\bar{1}$, $a = 9.270(5)$, $b = 12.760(6)$, $c = 20.07(1)$ Å, $\alpha = 98.66(5)$, $\beta = 98.28(5)$, $\gamma = 107.05(5)°$, $V = 2\,198.6$ Å^3, D_c 1 557 kg m^{-3}, $Z = 4$, $F(000) = 1\,052$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 11.8 cm^{-1}. Crystal dimensions 0.15 × 0.1 × 0.05 mm.

Data collection and processing. CAD4 diffractometer, graphite-monochromated Mo-K_α radiation, $\theta - 2\theta$ scan technique up to $2\theta = 50°$. The intensity fluctuations were random. Out of 7 710 measured reflexions only 2 544 had intensities higher than $2\sigma(I)$. No correction was applied for absorption.

The i.r. spectrum was recorded on a Perkin-Elmer 225 spectrometer in a Nujol mull on caesium iodide plates, and the solid-state reflectance spectrum on a Backman DK 2A spectrometer.

Structure Analysis.—A detailed examination of the three-dimensional Patterson synthesis did not allow the cobalt atoms to be located. A major difficulty appeared to result from the presence of two molecules in the asymmetric unit. With the multisolution technique[1] (500 E values $\geqslant 1.4$) two $CoCl_2$ molecular fragments could be observed. The 54 heavy atoms of the ligands were located by heavy-atom procedures. After a full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the N(3′)–C(10′) distance converged to a value of 0.7 Å, in molecule (**B**). In a difference Fourier synthesis, calculated for S(1′), N(3′), and C(10′), two distinct peaks appeared at each site for S(1′) and N(3′) indicating two possible orientations for the benzothiazoline part of one of the ligands. The carbon atoms of the benzothiazoline were located at the mean positions of each molecular orientation.

Least-squares refinement of the atomic parameters, and the occupation factors of S(1′), N(3′), and C(10′), converged to a statistical distribution of 60 and 40% for each orientation of the benzothiazolines part of molecule (**B**). 35 Out of 38 hydrogen atoms were located from a difference synthesis. Anomalous dispersion corrections for Co, Cl, and S were added,[2] and the refinement restarted with heavy atoms treated anisotropically, keeping the S(1′), N(3′), C(10′), and H positions and isotropic thermal parameters fixed. The contribution of the disordered 10′-methyl hydrogen atoms was omitted in the final refinement. The weighting function was, for $1 < |F| \leqslant 3.6$, $w = 1/0.47$, and for $3.6 < |F| \leqslant 35.5$, $w = (0.32 - 0.014\,84F_o + 0.0024F_o^2 - 0.000\,04F_o^3)^{-1}$. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.09, and the weighted residual $R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma wF_o^2\}^{1/2}$ was 0.10. The parameters shifts were $<0.1\sigma$, and the standard deviation of an observation of unit weight $S = [(\Sigma w||F_o| - |F_c||)^2/(m - n)]^{1/2}$ was 1.07 for 2 544 observations and 514 refined parameters. The scattering factors for the heavy atoms were from ref. 3 and for H from ref. 4. The final atomic parameters along with their e.s.d.s are given in Table 1 for the heavy atoms, and in Table 2 for the H atoms.

Results and Discussion

In the low region of the i.r. spectra broad and ill defined bands are recorded. The bands observed at 446 and 226 cm^{-1} were assigned to Me–O and Me-bridging ligand vibrations[5] respectively. The C–O frequency of acetone appears at 1 685 cm^{-1}. It is lowered by *ca.* 30 cm^{-1} with respect to the C–O vibrations of the free acetone molecule indicating that the molecule of acetone is not a cocrystallized solvent but a ligand.

In the solid-state reflectance spectra, absorption bands at 17 800, 16 900(sh), 16 200, 15 350(sh), 9 220, 6 000(sh), 4 780(sh), 4 350, and 4 120 cm^{-1} were observed. Bands between 4 120 and 6 000 cm^{-1} were attributed to the absorption of the ligand. The bulky peaks at 9 200 and 16 000 cm^{-1} probably result from the superposition of spectra of several complex species present in the solid state.

The *X*-ray crystal structure analysis revealed two molecules in the asymmetric unit, one in the form of a dimer (**A**) and the other in the form of a monomeride (**B**). In both molecules the co-ordination sphere of the Co atom is composed of oxygen and chlorine atoms. The bond angles θ along with their e.s.d.s and the dihedral angles δ, formed by the normals to two adjacent faces which share a common edge, as well as the corresponding angular deviations from the idealized tetragonal pyramidal and trigonal bipyramidal models are given in Tables 3 and 4, respectively. The angular values for the idealized co-ordination sphere are those given by Zemann[6] for the bond angles, and by Muetterties and Guggenberger[7] for the dihedral angles. The atomic numbering, and the designation of edges associated with the dihedral angles of the co-ordination polyhedron are given in Figure 1.

If the magnitude of the mean angular deviation from the idealized model is to be taken as a measure of the extent to which the stereochemistry of the co-ordination geometry of the cobalt atom approaches the idealized polyhedron, then the trigonal bipyramidal chacracter of $CoCl_3O_2$ (**A**) would be 42.4% and that of $CoCl_2O_3$ (**B**) 77.8%.[8]

Table 1. Fractional atomic co-ordinates (× 10^4)

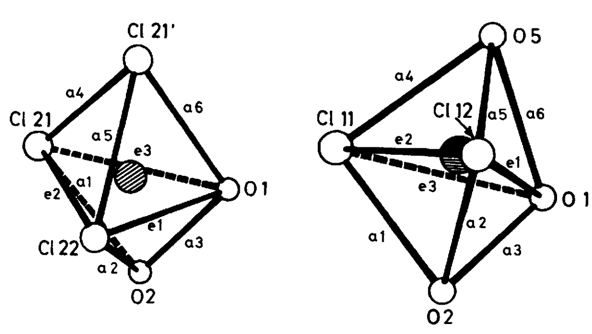
Molecule (**A**)	*x*	*y*	*z*
Co(2)	9 103(5)	5 659(2)	4 492(1)
Cl(21)	11 148(6)	6 225(4)	5 438(3)
Cl(22)	9 954(7)	5 953(5)	3 529(3)
S(1′)	5 382(6)	4 515(5)	2 764(3)
C(22′)	4 636(21)	3 908(16)	3 408(9)
N(3′)	5 191(17)	3 011(14)	3 467(10)
C(9′)	6 144(20)	2 843(17)	3 029(10)
C(4′)	6 766(21)	1 949(16)	3 008(12)
C(5′)	7 660(26)	1 939(21)	2 553(16)
C(6′)	7 979(24)	2 718(23)	2 130(12)
C(7′)	7 391(25)	3 576(20)	2 175(13)
C(8′)	6 404(22)	3 617(16)	2 604(11)
C(10′)	4 820(21)	2 366(16)	3 960(11)
C(3)	3 478(18)	4 163(17)	3 704(11)
C(4)	3 573(20)	5 209(16)	3 978(11)
C(4a)	4 861(22)	6 266(15)	4 163(10)
C(5)	4 475(24)	7 211(17)	4 101(11)
C(6)	5 588(23)	8 259(16)	4 301(12)
C(7)	7 151(21)	8 390(14)	4 500(10)
C(8)	7 520(21)	7 456(14)	4 562(10)
C(8a)	6 435(20)	6 334(15)	4 369(8)
C(11)	1 878(24)	3 221(20)	3 581(13)
O(1)	6 937(12)	5 493(9)	4 391(6)
O(2)	9 001(14)	7 439(10)	4 767(8)
C(9)	10 240(23)	8 482(17)	5 067(13)
N	5 151(25)	9 235(17)	4 171(12)
O(3)	6 189(20)	10 153(13)	4 315(12)
O(4)	3 828(22)	9 134(14)	3 977(12)
Molecule (**B**)			
Co(1)	−1 834(3)	7 383(2)	985(2)
Cl(11)	−2 248(7)	5 546(4)	985(3)
Cl(12)	−3 679(6)	8 191(5)	1 049(4)
S(1′)	3 102(7)	8 806(6)	1 846(4)
S(1″)	2 432(14)	7 188(10)	246(7)
C(22′)	2 838(18)	8 473(16)	903(12)
N(3′)	2 506(20)	7 488(16)	573(10)
N(3″)	3 064(18)	8 126(14)	1 421(9)
C(10′)	2 345(16)	7 162(12)	−156(8)
C(10″)	3 161(61)	8 985(45)	2 031(29)
C(9′)	2 477(27)	7 212(25)	1 630(22)
C(4′)	2 298(26)	6 753(23)	2 214(17)
C(5′)	1 853(29)	5 550(23)	2 054(16)
C(6′)	1 555(30)	4 971(20)	1 404(15)
C(7′)	1 831(28)	5 484(26)	870(15)
C(8′)	2 210(27)	6 636(35)	969(19)
C(3)	3 213(20)	9 554(15)	624(10)
C(4)	2 344(19)	9 692(15)	73(11)
C(4a)	781(17)	9 014(15)	−327(10)
C(5)	437(23)	9 182(14)	−998(11)
C(6)	−1 033(21)	8 580(16)	−1 403(12)
C(7)	−2 138(21)	7 836(15)	−1 146(11)
C(8)	−1 771(19)	7 680(15)	−493(10)
C(8a)	−335(16)	8 312(14)	−37(11)
C(11)	4 729(19)	10 522(16)	1 021(12)
O(1)	−139(12)	8 218(10)	606(7)
O(2)	−2 703(13)	6 951(11)	−172(7)
C(9)	−4 266(21)	6 325(18)	−547(13)
N	−1 389(22)	8 831(15)	−2 077(11)
O(4)	−378(20)	9 326(13)	−2 331(8)
O(3)	−2 800(17)	8 472(13)	−2 346(8)
O(5)	−642(15)	8 033(11)	1 995(8)
C(12)	−1 020(27)	8 063(19)	2 541(13)
C(13)	−2 696(37)	7 437(32)	2 618(19)
C(14)	−23(38)	8 741(19)	3 194(14)

Table 2. Fractional co-ordinates ($\times 10^3$) for hydrogen atoms

Molecule (**A**)	*x*	*y*	*z*
H(7′)	797	422	188
H(6′)	891	281	188
H(5′)	813	133	266
H(4′)	641	125	328
H(111)	188	297	312
H(112)	156	359	391
H(113)	195	297	406
H(101)	406	172	375
H(102)	399	281	406
H(103)	500	266	438
H(4)	297	555	438
H(5)	414	758	438
H(7)	789	906	453
H(91)	1 000	883	469
H(92)	1 117	820	500
H(93)	1 000	859	557
Molecule (**B**)			
H(4′)	156	703	234
H(5′)	141	521	242
H(6′)	156	422	141
H(7′)	141	523	31
H(111)	359	1 016	117
H(112)	500	1 102	70
H(113)	547	1 031	78
H(4)	266	1 047	−8
H(5)	117	992	−109
H(7)	−281	719	−156
H(91)	−359	600	−86
H(92)	−453	672	−78
H(93)	−422	555	−70
Acetone			
H(131)	656	726	234
H(132)	750	821	302
H(133)	789	688	273
H(141)	1 000	813	344
H(142)	1 008	945	344
H(143)	1 094	875	305

Table 3. Bond angles (°) along with their e.s.d.s and the angular deviations from the idealized tetragonal pyramidal (TP) and trigonal bipyramidal (TBP) models

Bond angle Molecule (**A**)	Idealized TP	Observed value	Idealized TBP	Angular deviation from	
				TP	TBP
Cl(22)–Co–O(1)	104.1	111.6(4)	120	7.5	8.4
Cl(22)–Co–O(2)	104.1	93.0(4)	90	11.1	3.0
Cl(22)–Co–Cl(21′)	104.1	107.2(2)	90	3.1	17.2
Cl(22)–Co–Cl(21)	104.1	110.9(2)	120	6.8	9.1
O(1)–Co–Cl(21′)	86.6	96.5(4)	90	9.9	6.5
Cl(21)–Co–Cl(21′)	86.6	88.2(2)	90	1.6	1.8
Cl(21)–Co–O(2)	86.6	85.3(4)	90	1.3	4.7
O(1)–Co–O(2)	86.6	74.6(5)	90	12.0	15.4
O(1)–Co–Cl(21)	151.9	133.5(4)	120	18.4	13.5
O(2)–Co–Cl(21′)	151.9	159.8(4)	180	7.9	20.2
$\Sigma\lvert\theta_{\mathrm{TBP}} - \theta_{\mathrm{TP}}\rvert = S$		133.6			
$\Sigma\lvert\theta_{\mathrm{OBS}} - \theta_{\mathrm{TBP}}\rvert = A$		99.8			
$\Sigma\lvert\theta_{\mathrm{OBS}} - \theta_{\mathrm{TP}}\rvert = A'$		79.6			
$S - A' = B$		54.0			
$(A + B)/2 = C$		76.9			
$100(1 - C/S)$		42.4%			
Molecule (**B**)					
O(2)–Co–Cl(11)	86.6	89.5(4)	90	2.9	0.5
O(2)–Co–O(1)	86.6	74.7(5)	90	11.9	15.3
O(2)–Co–Cl(12)	104.1	86.7(4)	90	17.4	3.3
O(5)–Co–Cl(11)	86.6	98.4(4)	90	11.8	8.4
O(5)–Co–Cl(12)	104.1	96.7(5)	90	7.4	6.7
O(5)–Co–O(1)	86.6	93.1(6)	90	6.5	3.1
Cl(11)–Co–Cl(12)	104.1	123.0(3)	120	18.9	3.0
Cl(11)–Co–O(1)	151.9	120.1(4)	120	31.8	0.1
O(1)–Co–Cl(12)	104.1	113.5(4)	120	9.4	6.5
O(2)–Co–O(5)	151.9	167.7(6)	180	15.8	12.3
$\Sigma\lvert\theta_{\mathrm{TBP}} - \theta_{\mathrm{TP}}\rvert = S$		133.6			
$\Sigma\lvert\theta_{\mathrm{OBS}} - \theta_{\mathrm{TBP}}\rvert = A$		59.2			
$\Sigma\lvert\theta_{\mathrm{OBS}} - \theta_{\mathrm{TP}}\rvert = A'$		133.8			
$S - A' = B$		0.2			
$(A + B)/2 = C$		29.7			
$100(1 - C/S)$		77.8%			



(a) (b)

Figure 1. Atomic numbering and dihedral angle designation of the cobalt atom co-ordination sphere: (a) dimer, (b) monomeride

The comparison of the observed dihedral angles with the corresponding values of idealized models confirms the results obtained from the bond angle calculations: 41.0% trigonal bipyramidal character for (**A**) and 71.5% for (**B**).[8]

The value of δe_3, which by diminishing from 53.1 to 0° characterizes a triangular face approaching a square face, was 46.3° for the monomeride and 19.8° for the dimer.

The Co atom displacement from the trigonal bipyramid basal plane is 0.243(3) Å in (**A**) and 0.231(3) Å in (**B**). The distance from Co to the tetragonal pyramidal basal plane in (**A**) is 0.615(3) Å in the direction of Cl(22) as apical ligand.

The room-temperature magnetic moment of the complex was measured as 4.5 μB. The high-spin electronic configuration results in greater electron pair repulsion of the *d*-shell of the axial ligand, hence an increase of the apical bond lengths. The Co–O(5) bond is 2.08(2) Å and the Co–O(2) bonds are 2.27(1) and 2.29(1) Å with respect to the Co–O(1) equatorial bond, 1.93(1) and 1.95(1) Å, in (**A**) and (**B**) respectively. The Co–Cl equatorial bond lengths of 2.250(7), 2.261(6), 2.338(6), and 2.232(7) Å can be compared with the value of the average standard five-co-ordinate Co–Cl bond length (2.31 Å) in high-spin complexes.[10] The apical Co–Cl′ bond, a bridging bond as well, is 2.375(6) Å. There is no interaction between the metal atoms in the dimer, the Co ··· Co distance being 3.385(4) Å.

Ligand Geometry.—A perspective view of the ligand with the atomic numbering is given in Figure 2(a). The bond lengths and angles are in Figures 2(b) and (c). The molecular geometry of the ligand can be associated with that of the hypothetical inter-

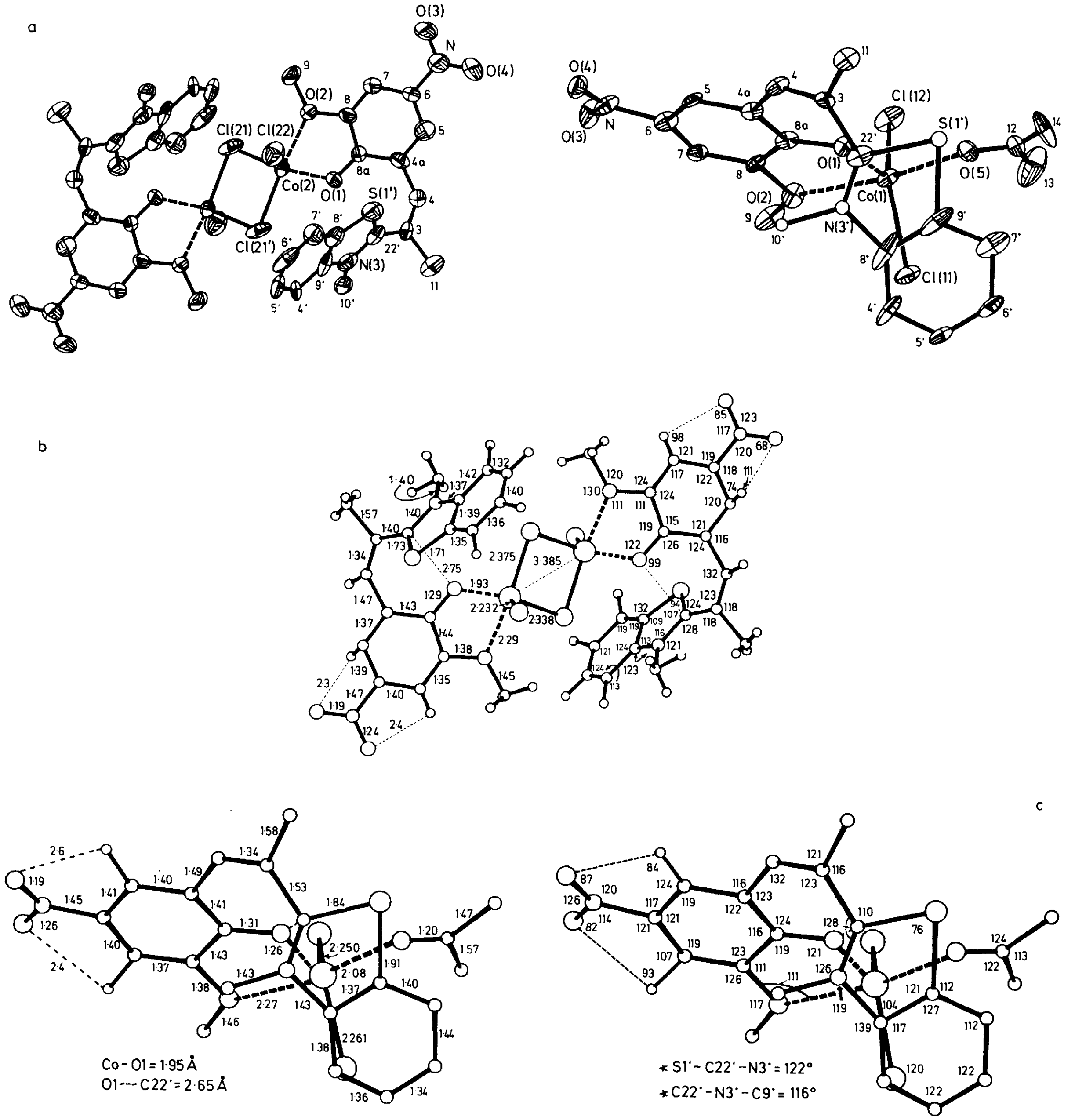


Figure 2. (a) Perspective view and atomic numbering of the compound. (b) Bond lengths (Å). The e.s.d.s are: 0.02 for C–S and C–O; 0.03 for C–C, C–N, and N–O; 0.013 for Co–O and 0.006 Å for Co–Cl in (A). 0.04 for C–C; 0.03 for C–O, C–N, C–S, and N–O; 0.014 for Co–O and 0.007 Å for Co–Cl in (B). (c) Bond angles (°). The e.s.d.s are 2° for C–C–C, C–C–N, C–N–O, and O–N–O; 1.5° for C–C–O, C–C–S, N–C–S in (A). 2° for C–C–C, C–C–O, C–N–O, N–C–S, O–N–O, and C–C–N; 2.7° for C–C–S in (B)

mediate of the spiropyran $\rightleftharpoons$ merocyanine photochemical transformation process. The C(22′)–O(1) distances of 2.65(2) Å in (**B**) and 2.75(2) Å in (**A**) are lying between a C_{sp^3}–O bond length (1.44 Å) and the C ··· O van der Waals contact (3.1 Å). The ligands maintain a bent conformation, the dihedral angle between the phenyl ring and benzothiazoline plane being 115 and 125° in (**A**) and (**B**), respectively. The C(22′)–S(1′) and C(22′)–C(3) bond lengths in (**B**), 1.84(3) and 1.53(3) Å, respectively, could suggest an sp^3-hybridized C(22′) atom if its positional parameters did not represent the average position in the two statistically distributed benzothiazolines in (**B**). In molecule (**A**) the C(22′)–S(1′) and C(22′)–C(3) bonds, 1.73(2) and 1.39(3) Å, respectively, favour an sp^2-hybridized C(22′) atom. The bond angles and bond lengths of the methine chain and of the phenyl ring agree with those observed in the thiazolidine spiropyran (TSP).[11]

In each ligand molecule the benzothiazoline ring is planar, with the exception of C(7′) which is at 0.10(3) Å from the least-squares plane. The C(22′) atom is 0.09(2) Å [in (**A**)] and 0.04(2) [in (**B**)] from the plane passing through S(1′), N(3′), and C(3). The phenyl rings are also planar.

The distances (Å) of the phenyl ring substituents from the least-squares plane of the ring are as follows:

	(A)	(B)		(A)	(B)
O(1)	0.09(1)	−0.17(1)	N	0.14(2)	−0.13(2)
O(2)	−0.01(2)	0.09(1)	O(3)	0.18(2)	−0.45(2)
C(9)	−0.22(2)	0.03(2)	O(4)	0.15(2)	0.07(2)

Table 4. Dihedral angles and the angular deviations (°) from the idealized tetragonal pyramidal (TP) and trigonal bipyramidal (TBP) models

Shape determining angle	Idealized TBP	Observed values for TBP	Idealized TP	Observed values for TP	Angular deviation from TBP	TP
Molecule (**A**)						
δe1	53.1	60.3	75.7	60.3	7.2	15.4
δe2	53.1	61.5	75.7	61.5	8.4	14.2
δe3	53.1	19.8	0.0	19.8	33.3	19.8
Remaining angles						
δa1	101.5	102.0	119.8	122.3	0.5	2.5
δa3	101.5	108.0	119.8	114.0	6.5	5.8
δa4	101.5	117.1	119.8	122.4	15.6	2.6
δa6	101.5	110.2	119.8	110.2	8.7	9.6
δa2	101.5	60.0	75.7	60.0	41.5	15.7
δa5	101.5	86.1	75.7	86.1	15.4	10.4
$\Sigma\lvert\delta_{TBP} - \delta_{OBS}\rvert = A$		137.1		$S - A' = B$		130.5
$\Sigma\lvert\delta_{TP} - \delta_{OBS}\rvert = A'$		96.0		$(A + B)/2 = C$		133.8
$\Sigma\lvert\delta_{TBPideal} - \delta_{TPideal}\rvert = S$		226.5*		$100(1 - C/S)$		41%
Shape determining angle						
Molecule (**B**)						
δe1	53.1	47.7	75.7	47.7	5.4	28.0
δe2	53.1	61.7	75.7	61.7	8.6	14.0
δe3	53.1	46.3	0.0	46.3	6.8	46.3
Remaining angles						
δa1	101.5	102.5	119.8	125.5	1.0	5.7
δa3	101.5	99.5	119.8	104.8	2.0	15.0
δa4	101.5	107.2	119.8	125.9	5.7	6.1
δa6	101.5	99.8	119.8	103.2	1.7	16.6
δa2	101.5	99.8	75.7	80.2	1.7	4.5
δa5	101.5	104.3	75.7	75.7	2.8	0.0
$\Sigma\lvert\delta_{TBP} - \delta_{OBS}\rvert = A$		35.7		$S - A' = B$		97.3
$\Sigma\lvert\delta_{TP} - \delta_{OBS}\rvert = A'$		136.2		$(A + B)/2 = C$		66.5
$\Sigma\lvert\delta_{TBPideal} - \delta_{TPideal}\rvert = S$		233.5*		$100(1 - C/S)$		71.5%

The individual dihedral angles, δ, are identified with reference to the common edges shared by two adjacent traingular faces (Figure 1).

* The sums of the dihedral angle changes between idealized TBP and TP geometries, 226.5 and 233.5°, correspond to transbasal angles of 160 [in (**A**)] and 167.7° [in (**B**)] respectively.[9]

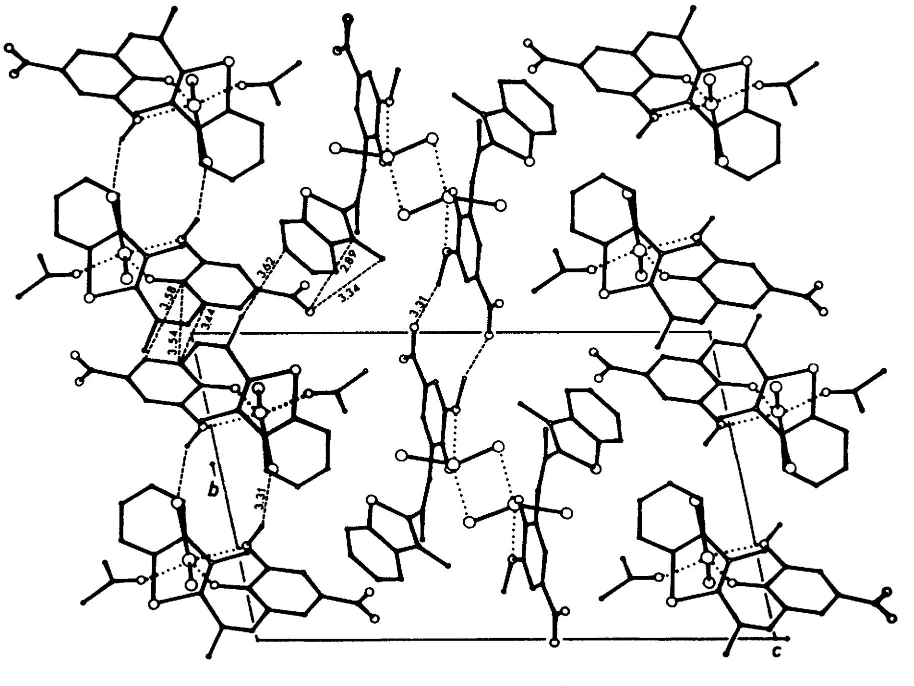


Figure 3. Molecular packing of the title compound viewed along *a* (distances in Å)

Table 5. Conformational parameters. The e.s.d.s in parentheses apply to the last significant digit

Pyran ring torsion angles (°)	(A)	(B)	TSP
C(3)–C(22′)–O(1)–C(8a)	49(1)	52(1)	44.6(2)
C(22′)–O(1)–C(8a)–C(4a)	−26(1)	−34(1)	26.4(2)
O(1)–C(8a)–C(4a)–C(4)	−3(1)	3(1)	−4.2(2)
C(8a)–C(4a)–C(4)–C(3)	29(2)	26(2)	14.4(2)
C(4a)–C(4)–C(3)–C(22′)	13(2)	11(2)	6.5(2)
C(4)–C(3)–C(22′)–O(1)	−38(1)	−37(1)	34.5(2)

In Table 5 the 'opened' pyran ring torsion angles are compared with those of pyran ring of TSP. The torsion angles of all the three molecules, (**A**), (**B**), and TSP, are of the same order of magnitude, except for the values of the C(4)–C(4a) bond. In (**A**) and (**B**) it is doubled, 29(2) and 26(2)°, with respect to the corresponding value in TSP, 14.4(2)°. It is mainly about this bond that straightening of the spiropyran occurs during the spiropyran ——→ merocyanine transformation. The 'opened' pyran ring conformation is still a screw-boat as in TSP. The values of φ_2 and θ^{12} are 340(3) and 65(3)° in (**A**), 338(3) and 63(3)° in (**B**), 347.3(5) and 69.2(5)° in TSP. (The calculated values for a screw-boat conformation are φ_2 330 and θ 67.5°.[13]) The C(22′) and O(1) atoms are on the opposite sides of the plane passing through C(3), C(4), C(4a), C(8a) at 0.74(2) and 0.29(1) Å in (**A**), 0.71(2) and 0.37(1) Å in (**B**), and 0.431(2) and 0.127(2) Å in TSP.

In (**A**) the chelate ring conformation is a nearly perfect envelope with the Co atom at the flap, 0.401(2) Å from the plane passing through O(1), O(2), C(8a), and C(8). The puckering coefficients q_2 and φ_2 are 0.19(3) Å and 186(3)°. ΔC_s [Co] is 1(2)°. The chelate ring conformation in (**B**) is twist with Co and O(2) on opposite sides of the plane passing through O(1), C(8a), C(8), at 0.221(3) and 0.143(1) Å respectively. The puckering parameters q_2 and φ_2 are 0.19(3) Å and 16(3)°, ΔC_2 [Co–O(2)] being 2(2)°.

Molecular Packing.—The molecular packing is illustrated in Figure 3. The monomeride complex is piled up in stacks along the *b*-axis. Adjacent molecules, reversed in orientation, associate across inversion centres at 0,0,0. Within these pairs van der Waals contacts are established between C(4a) ··· C(4a)^{ii} [3.44(3) Å], C(4a) ··· C(8a)^{ii} [3.54(3) Å], C(5) ··· C(8a)^{ii} [3.58(3) Å], and C(7) ··· C(11)^{i} [3.63(3) Å]. Short C(9) ··· Cl contacts of 3.31(2) Å are further observed. The second molecule in the asymmetric unit dimerizes across the inversion centre at 0,1/2,1/2 and piles up along the *a*-axis. A short contact of 3.31(3) Å between O(3) and C(9)^{i} is the link between the stacks of dimers. The molecules are further cross-linked through van der Waals contacts between the benzothiazoline atoms of the dimer and the phenyl ring and methine chain substituents of the monomeric complex:

C(10′) (**A**) ··· O(4) (**B**)^{i} 3.34(3) Å, N(3′) (**A**) ··· O(4) (**B**)^{i} 2.89(2) Å C(6′) (**A**) ··· C(11) (**B**) 3.62(4) Å
i = 1 − *x*, 1 − *y*, 1 − *z*
ii = 1 − *x*, 2 − *y*, 1 − *z*

References

1 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.
2 D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, 1970, **53**, 1891.
3 D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 1965, **18**, 104.
4 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
5 G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.
6 J. Zemann, *Z. Anorg. Chem.*, 1963, **324**, 241.
7 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748.
8 R. R. Holmes and J. A. Dieters, *J. Am. Chem. Soc.*, 1977, **99**, 3318.
9 R. R. Holmes, *J. Am. Chem. Soc.*, 1984, **106**, 3745.
10 L. Sacconi, *Coord. Chem. Rev.*, 1972, **8**, 351.
11 E. Miler-Srenger and R. Guglielmetti, *Acta Crystallogr., Sect. C*, 1984, **40**, 2050.
12 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.
13 J. C. A. Boyens, *J. Cryst. Mol. Struct.*, 1978, **8**, 317.

Received 23*rd June* 1986; *Paper* 6/1265