Structures of Three Diastereomers of *trans*(*N*-Ph, *N*-Ph)-2,4-Pentanedionatobis-(*N*-phenylethylenediamine)cobalt(III) and of One Diastereomer of *trans*(*N*-Ph, *N*-Ph)-Oxalatobis(*N*-phenylethylene-diamine)cobalt(III) Complex Cations

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The molecular structures of three racemic pairs of diastereomers, *ΔRR*(*ΛSS*)-, *ΔSR*(*ΛRS*)-, and *ΔSS*(*ΛRR*)-*trans*(*N*-Ph, *N*-Ph)-[Co(pd)(Ph-en)$_2$]$^{2+}$ and of one racemic pair of diastereomers, *ΔSS*(*ΛRR*)-*trans*(*N*-Ph, *N*-Ph)-[Co(ox) (Ph-en)$_2$]$^+$ (pd=2,4-pentanedionate ion, ox=oxalate ion, Ph-en=*N*-phenylethylenediamine) were determined by the single-crystal X-ray diffraction method in order to study the intramolecular interactions between π-systems in the ligands. For the *ΔSS*(*ΛRR*)-isomer of [Co(pd)(Ph-en)$_2$]$^{2+}$, three kinds of crystal structures **3a**, **3b**, and **3c** were investigated. The crystal data and final *R* values are: *ΔRR*(*ΛSS*)-[Co(pd)(Ph-en)$_2$](ClO$_4$)$_2$·H$_2$O (**1**), orthorhombic, *Pbca*, *a*=32.472(9), *b*=11.120(3), *c*=15.303(4) Å, *V*=5526(3) Å^3, *Z*=8, *R*=0.065 for 2113 observed unique reflections. *ΔSR*(*ΛRS*)-[Co(pd)(Ph-en)$_2$](ClO$_4$)$_2$ (**2**), orthorhombic, $P2_12_12_1$, *a*=19.440(8), *b*=16.406(8), *c*=8.407(3) Å, *V*=2681(2) Å^3, *Z*=4, *R*=0.038 for 2205 reflections. *ΔSS*(*ΛRR*)-[Co(pd)(Ph-en)$_2$]-Cl$_2$·H$_2$O (**3a**), monoclinic, $P2_1/c$, *a*=12.475(3), *b*=11.590(2), *c*=19.054(4) Å, β=117.18(2)°, *V*=2450.6(9) Å^3, *Z*=4, *R*=0.035 for 2164 reflections. *ΔSS*(*ΛRR*)-[Co(pd)(Ph-en)$_2$](ClO$_4$)Cl·H$_2$O (**3b**), triclinic, $P\bar{1}$, *a*=11.847(5), *b*=13.584(4), *c*=8.367(2) Å, α=103.57(2), β=91.85(3), γ=84.25(3)°, *V*=1302.1(8) Å^3, *Z*=2, *R*=0.087 for 1374 reflections. *ΔSS*(*ΛRR*)-[Co(pd)(Ph-en)$_2$](ClO$_4$)Cl (**3c**), triclinic, $P\bar{1}$, *a*=11.660(5), *b*=14.028(3), *c*=8.308(7) Å, α=108.00(8), β=101.57(9), γ=92.47(13)°, *V*=1258(3) Å^3, *Z*=2, *R*=0.052 for 1118 reflections. *ΔSS*(*ΛRR*)-[Co(ox)(Ph-en)$_2$] Br·6H$_2$O (**4**), orthorhombic, $Pna2_1$, *a*=15.804(1), *b*=15.646(1), *c*=10.428(2) Å, *V*=2578.5(4) Å^3, *Z*=4, *R*=0.065 for 1496 reflectios. The numbers of phenyl rings of the Ph-en ligands that overlap with the pd π system in the complex cation are 0, 1, and 2 for **1**, **2**, and **3** respectively. The ox ligand of **4** is ill-sandwiched by the two phenyl rings, whereas the pd ligand is well-sandwiched in **3a**. The arrangements of the phenyl groups relative to the pd differ slightly from one another in the crystals of **3a**, **3b**, and **3c**. The dihedral angles between the pd (or ox) and phenyl rings range from 25 to 35°.

Three isomers of *trans*(*N*-Ph, *N*-Ph)-[Co(pd)(Ph-en)$_2$]$^{2+}$ were prepared and characterized.[1] Their absorption spectra are different from each other, although the structures differ simply in the absolute configurations of the coordinated secondary N atoms. The greater the number of Ph rings placed over the pd chelate ring, the lower the energy of the first absorption band.[1] X-Ray crystal structure analyses have been done to verify their relative configurations, as assigned on the basis of the ^{1}H NMR spectra, and to investigate the intramolecular interaction of the π systems. The *ΔSS*(*ΛRR*)-*trans*(*N*-Ph,*N*-Ph)-[Co(ox)(Ph-en)$_2$]$^+$ complex has also been prepared and its structure examined in order to compare the results with those for the pd complexes.

Experimental

Preparation of [Co(ox)(Ph-en)$_2$]Br·6H$_2$O. The procedure was carried out under an atmosphere of nitrogen until the complex was formed. To a deaerated solution (180 cm^3) of K$_3$[Co(ox)$_3$]·3H$_2$O (2.8 g, 7.1 mmol) in dimethyl sulfoxide-water (4:5 v/v) we added deaerated *N*-phenylethylenediamine (1 g, 7.34 mmol). The mixture was warmed at 30 °C for 3 h. The resulting dark purple solution was diluted with water (1500 cm^3) and placed in a column (φ2.8 cm ×20 cm) of Dowex 1×8 (Cl$^-$ form) to remove the anionic species. The column was then washed with water, and the red effluent was placed in a column (φ2.8 cm×20 cm) of Dowex 50W×8 (Na$^+$ form). By elution with 0.6 mol dm^{-3} NaBr-0.01 mol dm^{-3} HBr, two red bands and a brown band developed in this order, the brown one remaining at the top of the column. The eluate containing the fastest-moving red band (main band) was collected and evaporated to dryness under reduced pressure. The residue was shaken with methanol to extract the complex, and the solvent was removed under reduced pressure. The residue was dissolved in a small amount of 0.01 mol dm^{-3} HBr and then allowed to stand overnight in a refrigerator. The red crystals were collected by filtration and washed with water and then methanol. Yield: 0.93 g (23%). UV-VIS spectrum (0.01 mol dm^{-3} HBr) 18.55 (log ε 2.32), 28.59 (4.72), and 42.72×10^3 cm^{-1} (4.87).

The slower-moving red band seemed to contain another isomer (racemic pair of the diastereomers) of [Co(ox)(Ph-en)$_2$]$^+$. The complex was not isolated, however, since it was unstable and the amount was very small. The complex showed the first absorption band at 18870 cm^{-1}. The abundance of the first band relative to that of the second band was ca. 30:1 when the two isomers were assumed to have the same molar absorption coefficient.

Crystal-Structure Determination. Crystals of **1**, **2**, and **3** were grown from acetone-HCl and HClO$_4$ mixtures to avoid epimerization.[1] Compound **4** was recrystallized from water. The experimental conditions and refinement information are listed in Table 1. The intensities were measured using graphite monochromatized Mo*Kα* radiation (λ=0.71073 Å) on an automated Rigaku four-circle diffractometer AFC-5. The θ-2θ scan technique was employed at a scan rate of 6° min^{-1} in θ. The lattice constants were determined from

Table 1. Crystal Data, Experimental Conditions, and Refinement Details

	(1) *ΔRR*(*ΔSS*)-[Co(pd)-(Ph-en)$_2$]-(ClO$_4$)$_2$·H$_2$O	(2) *ΔSR*(*ΔRS*)-[Co(pd)-(Ph-en)$_2$](ClO$_4$)$_2$	(3) *ΔSS*(*ΔRR*)-[Co(pd)(Ph-en)$_2$]			(4) *ΔSS*(*ΔRR*)-[Co(ox)(Ph-en)$_2$]Br·6H$_2$O
			(a) Cl$_2$·H$_2$O	(b) (ClO$_4$)Cl·H$_2$O	(c) (ClO$_4$)Cl	
Formula weight	647.4	629.3	519.4	583.4	565.3	607.3
Space group and Z	*Pbca*, 8	$P2_12_12_1$, 4	$P2_1/c$, 4	$P\bar{1}$, 2	$P\bar{1}$, 2	$Pna2_1$, 4
D_m and D_x/Mg m^{-3}	1.55(1), 1.56	1.56(1), 1.56	1.41(1), 1.41	1.49(1), 1.49	1.49(1), 1.49	1.50(2), 1.56
μ(Mo $K\alpha$)/mm^{-1}	0.870	0.896	0.940	0.912	0.935	2.22
Color and shape of crystals	Brown-red prisms	Brown prisms	Green prisms	Brown prisms	Brown prisms	Orange-red prisms
Size of specimen/mm^3	0.20×0.20×0.40	0.18×0.18×0.60	0.12×0.25×0.28	0.20×0.20×0.25	0.05×0.10×0.20	0.20×0.36×0.50
$2\theta_{max}$/°	45	55	50	40	40	55
Range of h, k, and l	$0\leqq h\leqq 34$ $0\leqq k\leqq 11$ $0\leqq l\leqq 16$	$0\leqq h\leqq 25$ $0\leqq k\leqq 21$ $0\leqq l\leqq 10$	$0\leqq h\leqq 14$ $0\leqq k\leqq 13$ $-22\leqq l\leqq 22$	$-11\leqq h\leqq 11$ $-13\leqq k\leqq 13$ $-8\leqq l\leqq 0$	$-11\leqq h\leqq 11$ $-13\leqq k\leqq 13$ $0\leqq l\leqq 8$	$0\leqq h\leqq 20$ $0\leqq k\leqq 20$ $0\leqq l\leqq 13$
Systematic absences	*hk*0, *h* odd; 0*kl*, *k* odd; *h*0*l*, *l* odd	*h*00, *h* odd 0*k*0, *k* odd; 00*l*, *l* odd	*h*0*l*, *l* odd; 0*k*0, *k* odd	None	None	*h*0*l*, *h* odd; 0*kl*, *k*+*l* odd
Possible space groups	*Pbca*	$P2_12_12_1$	$P2_1/c$	*P*1 or $P\bar{1}$	*P*1 or $P\bar{1}$	$Pna2_1$ or *Pnam*
Variation in standard reflections $\sum(\lvert F_o\rvert/\lvert F_o\rvert_{initial})/n$	1.00—1.01 n=5	0.99—1.00 n=5	0.99—1.00 n=4	0.99—1.00 n=4	0.95—1.02 n=3	0.99—1.01 n=5
Number of reflections measured	4206	3475	4528	2789	2557	3127
Number of reflections observed [$\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$]	2113	2205	2276	1567	1228	1496
Transmission factor, A	0.584—0.825	0.718—0.792	0.779—0.904	0.836—0.870	No absorption correction	0.441—0.648
Number of unique reflections	2113	2205	2164	1374	1118	1469
Final R value	0.065	0.038	0.035	0.087	0.052	0.065
$(\Delta/\sigma)_{max}$ for nonhydrogen atoms	0.15	0.42	0.42	0.32	0.27	0.25
$\Delta\rho$/e Å^{-3}	−0.65, 0.68	−0.26, 0.32	−0.25, 0.37	−0.62, 0.72	−0.33, 0.37	−0.96, 0.32

Table 2. Fractional Coordinates (×10^4, ×10^5 for Co) and Equivalent Isotropic Thermal Parameters (×10)

Atom	x	y	z	$10B_{eq}$/Å^2	Atom	x	y	z	$10B_{eq}$/Å^2
1 Co	12899(4)	24007(13)	50373(10)	21	C(11)	1496(3)	−2096(10)	3679(8)	33
Cl(1)	613(1)	5193(3)	2554(2)	35	C(12)	1117(4)	−1917(11)	4079(9)	41
Cl(2)	2492(1)	995(3)	2309(2)	49	C(13)	1080(3)	−1006(10)	4666(8)	33
O(1)	761(2)	2442(7)	5529(5)	28	C(14)	1969(3)	3758(12)	4378(8)	39
O(2)	1120(2)	1868(6)	3919(4)	26	C(15)	1583(4)	4417(11)	4070(8)	37
O(11)	1015(3)	5669(10)	2702(8)	80	C(16)	1084(3)	4999(10)	5229(7)	23
O(12)	578(3)	5007(9)	1641(6)	60	C(17)	662(3)	5139(11)	5333(8)	33
O(13)	595(4)	4075(9)	3006(7)	80	C(18)	530(5)	5958(12)	5967(10)	62
O(14)	321(3)	6010(10)	2820(7)	82	C(19)	789(5)	6635(12)	6440(9)	52
O(21)	2646(4)	−74(13)	2619(8)	117	C(20)	1216(4)	6494(12)	6309(9)	49
O(22)	2309(4)	847(12)	1496(7)	97	C(21)	1358(4)	5661(12)	5704(8)	42
O(23)	2225(5)	1516(15)	2858(9)	150	O(W1)	2604(3)	1679(10)	5517(7)	70
O(24)	2831(4)	1765(14)	2115(11)	140					
N(1)	1499(3)	2889(8)	6187(6)	28	**2** Co	5458(4)	12719(4)	4949(9)	20
N(2)	1343(2)	716(8)	5491(5)	22	Cl(1)	3098(1)	12(1)	620(2)	32
N(3)	1840(2)	2463(8)	4536(6)	27	Cl(2)	471(1)	4242(1)	−1644(2)	36
N(4)	1220(2)	4103(8)	4588(6)	25	O(1)	−154(2)	1916(2)	−416(5)	28
C(1)	51(3)	2160(12)	5705(9)	42	O(2)	301(2)	1501(2)	2629(4)	25
C(2)	438(3)	2064(10)	5182(8)	30	O(11)	2747(3)	619(3)	−252(6)	53
C(3)	409(3)	1604(11)	4324(8)	35	O(12)	3316(3)	336(3)	2112(6)	54
C(4)	745(3)	1539(10)	3760(7)	24	O(13)	2642(3)	−652(4)	903(8)	74
C(5)	685(4)	1002(13)	2862(8)	44	O(14)	3677(3)	−291(4)	−203(6)	64
C(6)	1509(4)	1839(11)	6782(8)	35	O(21)	241(3)	3841(3)	−231(5)	53
C(7)	1629(3)	758(11)	6244(8)	33	O(22)	343(3)	5073(3)	−1539(7)	71
C(8)	1406(3)	−269(10)	4882(7)	25	O(23)	87(4)	3949(4)	−2979(7)	83
C(9)	1792(4)	−471(11)	4501(9)	39	O(24)	1142(3)	4060(4)	−1888(9)	85
C(10)	1830(4)	−1395(12)	3920(9)	43	N(1)	832(3)	1091(3)	−1716(6)	33

Table 2. (Continued)

Atom	x	y	z	$10B_{eq}$/Å^2
N(2)	1177(2)	2246(3)	423(6)	26
N(3)	1250(2)	540(3)	1292(6)	25
N(4)	−68(2)	287(3)	574(6)	23
C(1)	−1118(3)	2771(4)	−622(11)	47
C(2)	−601(3)	2337(3)	338(8)	28
C(3)	−606(3)	2398(4)	1984(8)	33
C(4)	−179(3)	1982(4)	3024(7)	28
C(5)	−276(4)	2076(5)	4796(8)	47
C(6)	1140(3)	1855(4)	−2319(8)	33
C(7)	1619(3)	2168(4)	−1042(8)	31
C(8)	1556(3)	2485(4)	1852(7)	25
C(9)	2149(3)	2084(4)	2288(8)	29
C(10)	2483(3)	2307(4)	3696(9)	39
C(11)	2224(4)	2925(4)	4597(9)	47
C(12)	1639(4)	3326(4)	4147(9)	46
C(13)	1300(3)	3104(4)	2756(9)	36
C(14)	1036(3)	−326(4)	1065(8)	30
C(15)	292(3)	−352(4)	1513(8)	33
C(16)	−788(3)	400(4)	1017(8)	27
C(17)	−1002(3)	333(4)	2597(9)	36
C(18)	−1684(4)	455(4)	2962(10)	49
C(19)	−2160(3)	654(5)	1807(12)	58
C(20)	−1936(4)	735(5)	226(11)	55
C(21)	−1266(3)	594(4)	−151(9)	37
3a Co	14243(5)	24661(6)	46879(3)	21
Cl(1)	1614(1)	−673(1)	7052(1)	48
Cl(2)	1895(1)	5876(1)	5601(1)	44
O(1)	2027(2)	1000(3)	5112(2)	25
O(2)	2861(3)	3023(3)	4709(2)	28
N(1)	−62(3)	1969(3)	4697(2)	27
N(2)	1904(3)	3113(3)	5778(2)	25
N(3)	676(3)	3931(3)	4221(2)	29
N(4)	882(3)	1943(3)	3563(2)	24
C(1)	3377(5)	−531(4)	5655(3)	43
C(2)	3103(4)	663(4)	5315(2)	28
C(3)	3973(4)	1316(4)	5232(3)	31
C(4)	3828(4)	2418(5)	4953(2)	31
C(5)	4844(5)	3052(5)	4904(4)	55
C(6)	176(4)	1855(4)	5531(3)	31
C(7)	860(4)	2922(4)	5952(3)	31
C(8)	3087(4)	2795(4)	6410(2)	24
C(9)	4052(4)	3492(4)	6547(3)	30
C(10)	5185(4)	3222(5)	7147(3)	39
C(11)	5340(4)	2277(4)	7619(3)	42
C(12)	4374(5)	1583(4)	7479(3)	41
C(13)	3235(4)	1832(4)	6871(3)	31
C(14)	−72(5)	3790(4)	3351(3)	39
C(15)	613(5)	3013(4)	3070(3)	36
C(16)	1631(4)	1113(4)	3424(2)	24
C(17)	2468(4)	1422(5)	3172(3)	39
C(18)	3169(5)	601(6)	3065(3)	53
C(19)	3048(5)	−527(6)	3213(3)	57
C(20)	2216(5)	−874(5)	3468(3)	42
C(21)	1496(4)	−37(4)	3563(3)	33
O(W)1[a]	−1491(6)	1155(6)	1339(4)	69
O(W)2	−2197(21)	704(21)	1203(13)	45
O(W)3	−1545(23)	1511(24)	1192(15)	61
3b Co	31068(21)	21976(19)	31008(34)	40
Cl(1)	6786(5)	2737(4)	7046(7)	62
O(1)	2128(8)	2361(8)	4852(13)	44
O(2)	2226(8)	3126(8)	2051(13)	41
O(11)	6433(17)	2342(12)	8298(21)	126
O(12)	6080(15)	2576(18)	5739(23)	168
O(13)	6814(29)	3745(12)	7595(24)	229
O(14)	7777(14)	2334(25)	6566(34)	229
N(1)	4021(11)	1232(10)	4094(20)	59
N(2)	2313(11)	1030(10)	1775(20)	56
N(3)	4172(12)	2053(11)	1336(18)	58
N(4)	4018(10)	3357(10)	4304(16)	39
C(1)	552(17)	2892(16)	6584(27)	73
C(2)	1182(13)	2952(12)	5082(21)	41
C(3)	766(13)	3557(12)	4030(20)	38
C(4)	1277(13)	3593(12)	2637(21)	37
C(5)	767(16)	4287(14)	1584(25)	60
C(6)	3585(19)	247(17)	3633(29)	87
C(7)	2779(20)	147(18)	2360(31)	98
C(8)	1100(14)	1141(12)	1654(21)	43
C(9)	687(15)	1476(14)	351(24)	56
C(10)	−539(19)	1663(17)	224(29)	86
C(11)	−1190(17)	1515(15)	1281(26)	68
C(12)	−879(18)	1153(17)	2545(28)	82
C(13)	354(17)	981(15)	2764(26)	73
C(14)	5084(17)	2761(15)	1823(26)	72
C(15)	4544(15)	3729(13)	3022(23)	54
C(16)	3466(13)	4163(12)	5589(21)	38
C(17)	2917(14)	5032(13)	5198(22)	46
C(18)	2436(15)	5775(13)	6500(23)	53
C(19)	2497(15)	5685(14)	8074(24)	57
C(20)	3031(17)	4810(15)	8439(26)	70
C(21)	3576(15)	3973(13)	7139(23)	52
Cl(2)A[b]	3766(16)	−19(15)	−1667(26)	33
Cl(2)B	3249(22)	500(20)	−2290(34)	29
Cl(2)C	3126(21)	1246(19)	−2087(33)	28
Cl(2)D	3827(20)	377(18)	−2090(31)	23
Cl(2)E	3880(46)	−140(42)	−1267(73)	31
Cl(2)F	3958(46)	1511(41)	−2321(71)	29
Cl(2)G	3621(56)	−921(50)	−3046(86)	33
Cl(2)H	2836(83)	962(73)	−1962(127)	31
Cl(2)I	3799(27)	−197(25)	−1019(42)	22
3c Co	31756(15)	28726(14)	15216(23)	21
Cl(1)	3908(3)	7855(3)	2479(5)	47
Cl(2)	6122(3)	5182(3)	3246(4)	40
O(1)	1890(6)	2510(6)	−449(9)	28
O(2)	2537(6)	2115(5)	2705(9)	24
O(11)	2980(8)	7351(8)	2835(13)	69
O(12)	4929(10)	7891(12)	3678(18)	140
O(13)	4098(11)	7391(10)	839(14)	111
O(14)	3690(14)	8830(8)	2597(19)	136
N(1)	3810(8)	3777(7)	393(12)	28
N(2)	2484(8)	4079(7)	2789(12)	25
N(3)	4588(7)	3233(7)	3452(11)	23
N(4)	4014(7)	1694(7)	463(12)	25
C(1)	41(11)	1811(10)	−2293(17)	40
C(2)	952(10)	1957(9)	−556(15)	26
C(3)	729(10)	1495(9)	577(15)	26
C(4)	1510(10)	1591(9)	2126(16)	30
C(5)	1209(11)	1044(10)	3303(17)	44
C(6)	3092(10)	4617(9)	516(15)	29
C(7)	2887(10)	4977(9)	2265(15)	29
C(8)	1225(10)	3983(8)	2759(15)	24
C(9)	880(10)	3772(9)	4113(15)	29
C(10)	−311(12)	3663(10)	4142(18)	50
C(11)	−1143(12)	3737(10)	2750(18)	47
C(12)	−816(12)	3926(10)	1456(19)	51
C(13)	356(11)	4069(9)	1372(16)	35
C(14)	5498(10)	2603(9)	2953(16)	33
C(15)	4909(11)	1569(9)	1926(16)	36
C(16)	3339(11)	760(9)	−748(16)	33
C(17)	3124(10)	598(9)	−2499(16)	35
C(18)	2479(11)	−324(9)	−3641(16)	38

Table 2. (Continued)

Atom	x	y	z	$10B_{eq}$/Å^2	Atom	x	y	z	$10B_{eq}$/Å^2
C(19)	2100(11)	−1029(10)	−3035(17)	42	N(4)	1245(8)	1580(9)	−785(13)	17
C(20)	2286(11)	−882(10)	−1277(17)	40	C(1)	1898(10)	3896(10)	−381(17)	16
C(21)	2931(10)	30(9)	−100(16)	33	C(2)	1193(11)	3609(12)	450(18)	28
					C(3)	1782(11)	437(11)	515(19)	27
4 Br	893(2)	1229(2)	3597(4)	75	C(4)	1011(10)	795(10)	−43(21)	21
Co	22072(12)	21607(13)	0[c]	13	C(5)	3873(10)	2415(10)	225(15)	15
O(1)	3199(6)	2662(6)	745(10)	14	C(6)	3736(12)	1770(11)	−886(19)	26
O(2)	2933(6)	1575(6)	−1083(11)	15	C(7)	3046(10)	914(10)	1786(17)	15
O(3)	4580(7)	2674(8)	489(13)	37	C(8)	3263(11)	1276(12)	2954(20)	28
O(4)	4322(7)	1457(8)	−1540(14)	31	C(9)	4056(14)	1106(13)	3464(26)	43
O(W1)	711(7)	2879(8)	7288(12)	29	C(10)	4583(12)	516(13)	2901(21)	35
O(W2)	966(9)	3170(10)	4730(13)	47	C(11)	4347(12)	145(11)	1858(20)	28
O(W3)	4009(9)	3990(9)	2366(16)	47	C(12)	3568(11)	323(12)	1246(19)	26
O(W4)	3242(10)	360(9)	−3196(17)	55	C(13)	2850(11)	3298(10)	−2074(17)	21
O(W5)	2258(10)	3918(10)	3208(14)	52	C(14)	3526(10)	3813(10)	−1785(17)	19
O(W6)	1497(9)	646(9)	−3382(15)	46	C(15)	4199(11)	3865(13)	−2655(18)	25
N(1)	2123(7)	3168(8)	−1191(13)	13	C(16)	4180(11)	3470(14)	−3705(23)	37
N(2)	1481(8)	2820(9)	1149(13)	17	C(17)	3536(14)	2975(13)	−4077(19)	38
N(3)	2253(9)	1153(8)	1226(13)	19	C(18)	2797(13)	2886(12)	−3207(19)	33

a) Population parameters of disordered H_2O: O(W1), 0.6; and O(W2) and O(W3), 0.2. b) Population parameters of disordered Cl^-: A, 0.20; B, C and D, 0.15; E and F, 0.07; G, 0.06; H, 0.04, and I, 0.11. c) This parameter was used to define the origin of the unit cell along *z* and is listed without e.s.d.

Table 3. Bond Lengths(Å) and Bond Angles(°)

	1	**2**	**3a**		**4**
Bond length (Å)					
Co-O(1)	1.876(7)	1.885(4)	1.884(3)	Co-O(1)	1.917(10)
Co-O(2)	1.893(6)	1.894(4)	1.888(4)	Co-O(2)	1.852(10)
Co-N(1)	1.962(9)	1.963(5)	1.949(4)	Co-N(1)	2.011(13)
Co-N(2)	2.005(9)	2.016(5)	2.025(4)	Co-N(2)	1.954(13)
Co-N(3)	1.945(7)	1.940(5)	1.946(3)	Co-N(3)	2.031(13)
Co-N(4)	2.027(9)	2.010(5)	2.023(4)	Co-N(4)	1.951(13)
O(1)-C(2)	1.248(12)	1.278(7)	1.277(5)	O(1)-C(5)	1.256(18)
O(2)-C(4)	1.295(12)	1.266(7)	1.285(6)	O(2)-C(6)	1.321(21)
N(1)-C(6)	1.481(15)	1.479(8)	1.483(7)	O(3)-C(5)	1.220(19)
N(2)-C(7)	1.481(13)	1.507(8)	1.500(7)	O(4)-C(6)	1.250(23)
N(2)-C(8)	1.453(14)	1.463(8)	1.463(5)	N(1)-C(1)	1.462(21)
N(3)-C(14)	1.519(16)	1.493(8)	1.494(6)	N(1)-C(13)	1.486(21)
N(4)-C(15)	1.463(15)	1.487(8)	1.498(6)	N(2)-C(2)	1.504(23)
N(4)-C(16)	1.466(14)	1.460(7)	1.447(7)	N(3)-C(3)	1.536(22)
C(1)-C(2)	1.494(15)	1.473(9)	1.500(6)	N(3)-C(7)	1.432(21)
C(2)-C(3)	1.412(17)	1.387(10)	1.390(8)	N(4)-C(4)	1.498(22)
C(3)-C(4)	1.393(15)	1.385(9)	1.363(7)	C(1)-C(2)	1.481(24)
C(4)-C(5)	1.511(17)	1.509(9)	1.504(9)	C(3)-C(4)	1.462(25)
C(6)-C(7)	1.508(17)	1.511(9)	1.508(6)	C(5)-C(6)	1.552(24)
C(8)-C(9)	1.401(16)	1.377(9)	1.372(7)	C(7)-C(8)	1.386(27)
C(8)-C(13)	1.379(15)	1.363(9)	1.380(7)	C(7)-C(12)	1.361(24)
C(9)-C(10)	1.364(19)	1.399(10)	1.388(6)	C(8)-C(9)	1.387(29)
C(10)-C(11)	1.386(17)	1.362(10)	1.374(8)	C(9)-C(10)	1.375(30)
C(11)-C(12)	1.389(17)	1.367(11)	1.370(8)	C(10)-C(11)	1.288(29)
C(12)-C(13)	1.359(17)	1.391(10)	1.393(6)	C(11)-C(12)	1.414(26)
C(14)-C(15)	1.527(17)	1.495(8)	1.499(9)	C(13)-C(14)	1.372(23)
C(16)-C(17)	1.388(14)	1.396(10)	1.381(8)	C(13)-C(18)	1.349(26)
C(16)-C(21)	1.365(17)	1.389(9)	1.384(7)	C(14)-C(15)	1.400(25)
C(17)-C(18)	1.398(19)	1.376(10)	1.369(9)	C(15)-C(16)	1.258(30)
C(18)-C(19)	1.341(21)	1.380(12)	1.360(10)	C(16)-C(17)	1.336(29)
C(19)-C(20)	1.410(21)	1.405(13)	1.391(10)	C(17)-C(18)	1.485(29)
C(20)-C(21)	1.388(19)	1.360(10)	1.389(8)		
Bond angle(°)					
O(1)-Co-O(2)	95.9(3)	95.3(2)	96.3(2)	O(1)-Co-O(2)	86.7(4)
O(1)-Co-N(1)	87.2(3)	84.5(2)	85.7(2)	O(1)-Co-N(1)	89.1(5)
O(1)-Co-N(2)	87.9(3)	89.0(2)	91.2(1)	O(1)-Co-N(2)	90.9(5)
O(1)-Co-N(3)	176.5(3)	175.1(2)	175.5(1)	O(1)-Co-N(3)	91.9(5)

Table 3. (Continued)

	1	2	3a		4
O(1)-Co-N(4)	90.6(3)	92.0(2)	93.4(1)	O(1)-Co-N(4)	176.0(5)
O(2)-Co-N(1)	176.2(3)	176.7(2)	176.8(2)	O(2)-Co-N(1)	93.0(5)
O(2)-Co-N(2)	92.6(3)	91.4(2)	91.1(2)	O(2)-Co-N(2)	177.4(5)
O(2)-Co-N(3)	85.5(3)	88.5(2)	87.9(2)	O(2)-Co-N(3)	88.7(5)
O(2)-Co-N(4)	87.3(3)	88.8(2)	88.8(2)	O(2)-Co-N(4)	89.8(5)
N(1)-Co-N(2)	85.3(4)	85.3(2)	86.4(2)	N(1)-Co-N(2)	85.8(5)
N(1)-Co-N(3)	91.5(3)	91.9(2)	90.1(2)	N(1)-Co-N(3)	178.1(5)
N(1)-Co-N(4)	94.8(4)	94.5(2)	93.5(2)	N(1)-Co-N(4)	93.1(5)
N(2)-Co-N(3)	95.2(3)	94.1(2)	90.1(1)	N(2)-Co-N(3)	92.6(5)
N(2)-Co-N(4)	178.5(4)	178.9(2)	175.4(2)	N(2)-Co-N(4)	92.6(6)
N(3)-Co-N(4)	86.3(3)	84.8(2)	85.3(1)	N(3)-Co-N(4)	86.0(5)
Co-O(1)-C(2)	126.2(7)	126.3(4)	124.3(3)	Co-O(1)-C(5)	113.1(10)
Co-O(2)-C(4)	122.2(6)	123.9(4)	123.1(3)	Co-O(2)-C(6)	112.7(11)
Co-N(1)-C(6)	109.9(7)	108.1(4)	108.1(3)	Co-N(1)-C(1)	105.7(10)
Co-N(2)-C(7)	107.1(6)	107.7(4)	107.0(3)	Co-N(1)-C(13)	116.0(10)
Co-N(2)-C(8)	119.6(6)	119.6(4)	117.7(3)	C(1)-N(1)-C(13)	116.1(12)
C(7)-N(2)-C(8)	115.8(8)	114.0(4)	115.6(4)	Co-N(2)-C(2)	108.3(10)
Co-N(3)-C(14)	110.5(7)	110.4(3)	109.7(3)	Co-N(3)-C(3)	104.2(10)
Co-N(4)-C(15)	108.5(7)	107.8(3)	106.7(3)	Co-N(3)-C(7)	119.4(10)
Co-N(4)-C(16)	116.2(7)	118.4(4)	117.5(3)	C(3)-N(3)-C(7)	115.5(12)
C(15)-N(4)-C(16)	116.3(9)	113.9(5)	114.4(4)	Co-N(4)-C(4)	110.9(10)
O(1)-C(2)-C(1)	117.1(10)	117.0(6)	114.4(4)	N(1)-C(1)-C(2)	106.5(13)
O(1)-C(2)-C(3)	125.0(10)	122.6(6)	124.5(4)	N(2)-C(2)-C(1)	107.7(14)
C(1)-C(2)-C(3)	117.9(9)	120.5(6)	121.1(4)	N(3)-C(3)-C(4)	108.5(14)
C(2)-C(3)-C(4)	122.9(10)	126.1(6)	125.7(5)	N(4)-C(4)-C(3)	108.3(13)
O(2)-C(4)-C(3)	127.3(10)	125.7(6)	126.0(5)	O(1)-C(5)-O(3)	125.2(15)
O(2)-C(4)-C(5)	113.8(9)	114.5(5)	112.9(5)	O(1)-C(5)-C(6)	113.8(14)
C(3)-C(4)-C(5)	118.9(9)	119.8(6)	121.1(5)	O(3)-C(5)-C(6)	120.8(14)
N(1)-C(6)-C(7)	107.4(10)	107.1(5)	106.5(4)	O(2)-C(6)-O(4)	122.4(16)
N(2)-C(7)-C(6)	106.7(9)	105.0(5)	109.9(4)	O(2)-C(6)-C(5)	113.6(15)
N(2)-C(8)-C(9)	120.9(10)	120.8(5)	118.4(4)	O(4)-C(6)-C(5)	124.0(16)
N(2)-C(8)-C(13)	119.6(9)	118.3(5)	121.3(4)	N(3)-C(7)-C(8)	117.9(15)
C(9)-C(8)-C(13)	119.5(10)	120.9(6)	120.3(4)	N(3)-C(7)-C12)	122.6(16)
				C(8)-C(7)-C(12)	119.4(16)
C(8)-C(9)-C(10)	118.2(11)	119.3(6)	119.9(4)	C(7)-C(8)-C(9)	118.8(18)
C(9)-C(10)-C(11)	121.8(12)	119.6(6)	120.3(5)	C(8)-C(9)-C(10)	120.8(21)
C(10)-C(11)-C(12)	119.7(11)	120.8(7)	119.5(4)	C(9)-C(10)-C(11)	119.2(19)
C(11)-C(12)-C(13)	118.5(11)	120.1(7)	120.8(5)	C(10)-C(11)-C(12)	123.0(18)
C(8)-C(13)-C(12)	122.2(10)	119.4(6)	119.1(4)	C(7)-C(12)-C(11)	118.3(17)
N(3)-C(14)-C(15)	106.1(9)	105.3(5)	107.0(4)	N(1)-C(13)-C(14)	123.1(15)
N(4)-C(15)-C(14)	112.3(9)	107.5(5)	105.9(5)	N(1)-C(13)-C(18)	115.4(15)
N(4)-C(16)-C(17)	116.8(9)	121.2(6)	123.0(5)	C(14)-C(13)-C(18)	121.4(17)
N(4)-C(16)-C(21)	121.8(9)	119.3(6)	117.4(5)	C(13)-C(14)-C(15)	118.9(16)
C(17)-C(16)-C(21)	121.5(10)	119.4(6)	119.6(5)	C(14)-C(15)-C(16)	121.2(19)
C(16)-C(17)-C(18)	117.1(11)	119.2(6)	120.5(6)	C(15)-C(16)-C(17)	123.8(20)
C(17)-C(18)-C(19)	123.2(14)	121.6(7)	119.9(6)	C(16)-C(17)-C(18)	118.4(18)
C(18)-C(19)-C(20)	118.5(13)	118.7(7)	121.4(7)	C(13)-C(18)-C(17)	116.2(18)
C(19)-C(20)-C(21)	119.7(13)	120.1(8)	118.3(6)		
C(16)-C(21)-C(20)	119.9(12)	121.0(7)	120.3(5)		

15—34 2θ values ($20<2\theta<30°$). Absorption corrections were made except for the small crystal of **3c**. The positions of the heavy atoms were determined from the Patterson function, while the other nonhydrogen atoms were located by means of Fourier syntheses and were refined anisotropically. The ratios of the number of H atoms located by the difference synthesis are **1** 24/31, **2** 24/31, **3a** 30/31, **3b** 16/31, **3c** 27/31, and **4** 12/24. The other H atoms were calculated and refined isotropically. The function, $\sum w||F_o|-|F_c||^2$, was minimized with $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ by the block-diagonal least-squares method. Complex neutral-atom scattering factors were used.[2] The calculations were carried out on a FACOM M380R computer at Keio University using the computation program system UNICS-III.[3] The final atomic parameters are listed in Table 2, and the bond lengths and bond angles within the complex cations, in Table 3.[4] The following points are worth mentioning. The structure of **1** is difficult to solve because the Co and two Cl atoms lie nearly on the glide planes, as shown in Fig. 1. The statistics of the intensity data showed that *hkl* with *h* or *l* odd is weak, suggesting pseudo translational symmetries of *a*/2 and *c*/2. The positions of the heavy atoms were determined by direct methods with MULTAN78[5] using a single overall scale factor in the normalization. The coordinated N and O atoms were deduced by means of Fourier synthesis utilizing the Co-ligand vectors found in the Patterson function. The

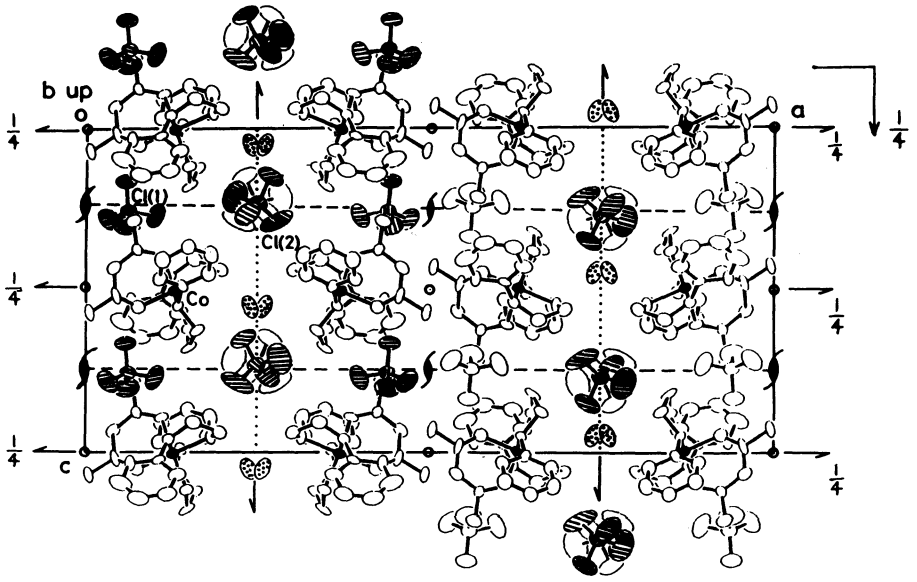

Fig. 1. A projection of the crystal structure of **1** along *b*.

space group of **2** is $P2_12_12_1$, indicating spontaneous resolution. The absolute structure was determined by anomalous-scattering techniques. The enantiomeric structure converged to R=0.0387 and wR=0.0449, slightly larger than the values of 0.0380 and 0.0441 for the adopted structure. In **3a**, the water molecules are disordered. The population parameters of three possible positions of O(W) were estimated by the trial-and-error method in such a way that the isotropic thermal parameter took nearly equal values. The Cl^- ion and water molecules in **3b** are disordered. The difference synthesis gave nine positions with peak heights greater than 1.0 e Å^{-3}. Since the disordered water molecules can not be distinguished from the disordered Cl^- ions, those peaks were tentatively assumed to be Cl^- ions and their population parameters were estimated by the trial-and-error method. The relatively large R value of **3b**, 0.087, may be attributed to this disorder. As the crystal of **3c** was too small to collect sufficient number of reflections, the carbon atoms were refined isotropically. The systematic absences of **4** indicated that the space group was $Pna2_1$ (No. 33) or the $a\bar{c}b$ setting of *Pnma* (No. 62). Since Z=4 and the complex cation has no mirror plane and no inversion center, the space group was determined to be $Pna2_1$.

Table 4. Short Intramolecular Distances (Å)

1	
C(17)···O(1)	3.031(14)
2	
C(16)···O(1)	3.026(7)
C(17)···C(4)	3.163(9)
C(21)···C(2)	3.165(8)
3a	
C(8)···O(1)	3.034(5)
C(9)···C(4)	3.174(7)
C(13)···C(2)	3.195(7)
C(16)···O(1)	3.026(6)
C(21)···C(2)	3.115(6)
4	
C(7)···C(5)	3.142(23)
C(12)···C(6)	3.184(27)
C(13)···C(5)	3.205(23)
C(13)···C(6)	3.035(24)
C(14)···C(5)	3.079(23)
C(18)···O(2)	3.026(22)

Results and Discussion

The atomic parameters of **1**, **3**, and **4** in Table 2 were selected to represent the absolute configuration *Δ* for convenience of comparison with **2**. The bond lengths and bond angles within the complex cations are listed in Table 3, while the short intramolecular distances and hydrogen bonds are listed in Tables 4 and 5 and

Table 5. Hydrogen Bonds (Distances in Å)

A···H-B (symmetry code)		A···B	A···H	H-B
1				
O(12)···H(N2)-N(2)	(i)	3.149(12)	2.22(9)	0.98(9)
O(22)···H(N1)1-N(1)	(i)	3.019(15)	2.17(8)	0.92(8)
2				
O(12)···H(N1)2-N(1)	(ii)	3.032(7)	2.05(7)	1.11(6)
O(14)···H(N3)2-N(3)	(iii)	2.979(7)	2.17(7)	0.85(7)
O(22)···H(N1)1-N(1)	(iv)	3.186(8)	2.12(5)	1.14(5)
3a				
Cl(1)···H(N4)-N(4)	(v)	3.146(4)	2.17(4)	0.98(4)
O(W)2···H(N3)2-N(3)	(vi)	3.14(3)	2.25(7)	1.01(6)
3b				
Cl(2)G···H(N1)2-N(1)	(vii)	2.92(7)	1.93(15)	0.98(14)
Cl(2)I···H(N3)2-N(3)	(vii)	3.27(3)	2.34(13)	1.04(12)
3c				
Cl(2)···H(N2)-N(2)	(vii)	3.19(1)	2.14(10)	1.07(11)
O(13)···H(N4)-N(4)	(viii)	3.04(2)	2.16(12)	0.96(12)
4				
O(W1)···H(N1)-N(1)	(ix)	2.77(2)	1.98(15)	0.80(15)

Symmetry code: (i) x, 1/2−y, z−1/2, (ii) 1/2−x, −y, z+1/2, (iii) 1/2−x, −y, z−1/2, (iv) −x, y+1/2, −z−1/2, (v) −x,−y, 1−z, (vi) −x, y−1/2, 1/2−z, (vii) 1−x, −y, −z, (viii) 1−x, 1−y, −z, (ix) x, y, z+1.

perspective drawings of the complex cations are presented in Fig. 2. The combinations of two asymmetric N atoms of the $[Co(pd)(Ph\text{-}en)_2]^{2+}$ complexes agree with the assignments based on the ^1H NMR spectra:[1] **1** *ΔRR*, **2** *ΔSR*, and **3** *ΔSS*. Only one of the diastereomers was isolated for the $[Co(ox)(Ph\text{-}en)_2]^{+}$ complex, the **4** *ΔSS* isomer. The two Ph-en ligands in the pd complexes take the lel ob conformation, which breaks the twofold symmetry of the *ΔRR* and *ΔSS* isomers. For the ox complex **4**, however, the Ph-en ligands take ob_2 configuration, which retains a twofold symmetry. The difference in the structures may be attributed to the difference in the O-Co-O chelate angles, 95.3(2)—96.3(2)° and 86.7(4)° for pd and ox respectively. The pd complexes are isomerized in a neutral aqueous solution with this equilibrium distribution ratio; *ΔRR*(*ΔSS*): *ΔSR*(*ΔRS*): *ΔSS*(*ΔRR*)=5 : 78 : 17 at 20 °C.[1] The N-Ph bonds in the most stable isomers **2** and **4** take a conformation equatorial to the en chelate ring. The Co atom lies almost on the pd or ox plane in each complex, in contrast to the bent Co-pd chelate ring in $(+)^{CD}_{531}$-[Co(pd)(RR-chxn)(edpp)]$(ClO_4)_2$.[6] The dihedral angles between the pd or ox chelate ring and phenyl groups range from 25 to 35° (see Table 6). There are no significantly close contacts between the phenyl groups and methyl groups of pd. Comparing

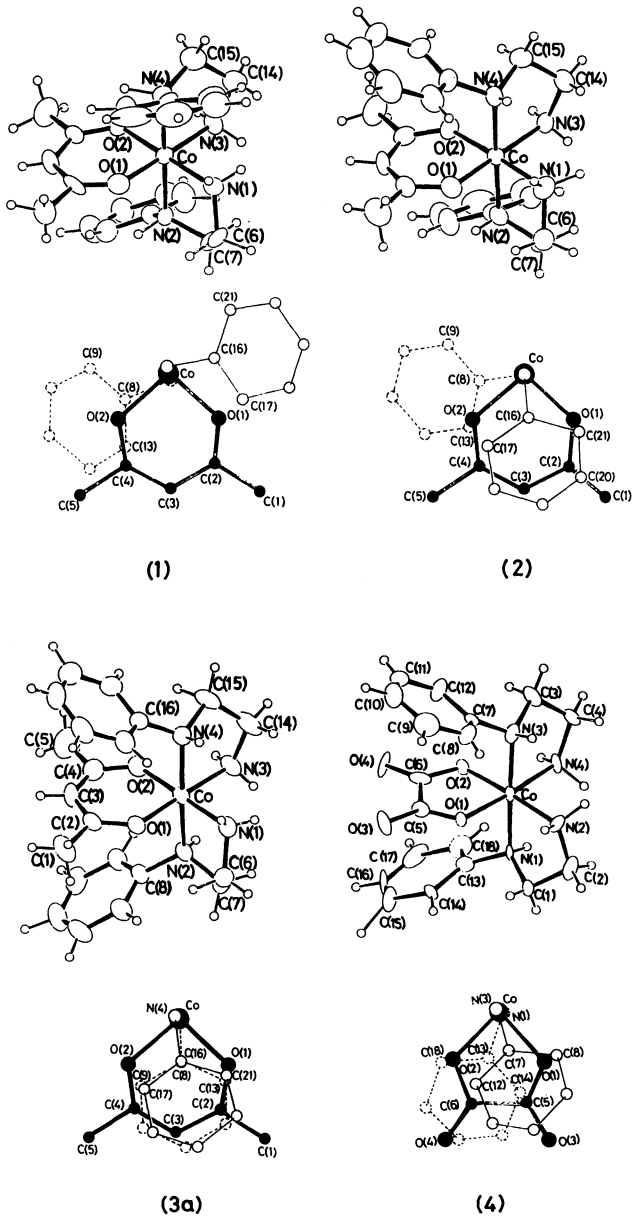

Fig. 2. Molecular structures, and projections of the Ph rings on the least squares plane through the pd or ox ligand for **1**, **2**, **3a**, and **4**. The Ph rings above and below the projection plane are drawn with solid and broken lines, respectively.

Table 6. Dihedral Angles (°) between the pd or ox Chelate Ring and Ph Rings Involving C(8) and C(16) Atoms

	C(8)	C(16)
1	25.6	27.9
2	28.7	29.8
3a	30.7	28.7
3b	27.5	33.5
3c	28.4	35.3
4	24.5	30.7

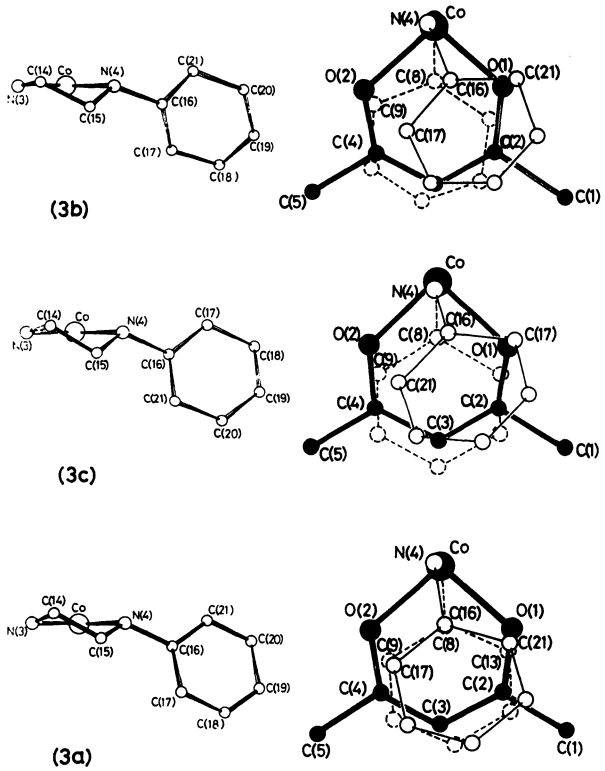

Fig. 3. Comparison of the Ph-en chelate ring conformations in *ΔSS*-$[Co(pd)(Ph\text{-}en)_2]^{2+}$ ions of **3b**, **3c**, and **3a**. The left half shows a projection along the line through the Co atom and the midpoint of the N(3)–N(4) axis. The right half shows a projection of the Ph rings on the pd chelate ring. The projections are arranged in a sequence that vividly illustrates the smooth change in the Ph-en chelate ring conformation in different crystal field.

the projections of the Ph rings to the least-squares plane through the pd in **3a** with that through the ox in **4** (see Fig. 2), the Ph rings of **3a** may be seen to overlap more with the pd π system than in **4**. However, the flexibility of the Ph-en chelate ring was revealed by the difference in the structures of **3a**, **3b**, and **3c**, as is shown in Fig. 3. The orientation of one of the Ph groups to the pd ligand alters with a different conformation of the five-membered chelate ring. After all, the orientation of the Ph group is altered along with the chelate-ring conformation of the Ph-en ligand, which is itself primarily determined by the coordination geometry around the Co atom. Molecular packing stabilization is a secondary condition, while the minor conditions are the intramolecular interactions between the π systems. The difference in the energy of the first absorption band of the three diastereomers of the pd complex[1] could not be explained by the structural data; no significant differences in the Co-N and Co-O bond lengths are observed among these diastereomers (see Table 3). The Co-N(HPh) bond distance is longer than the Co-N(H_2) distance by 0.06—0.07(1) Å, which corresponds to the fact that the ligand-field strength of Ph-en is weaker than that of en.[7]

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