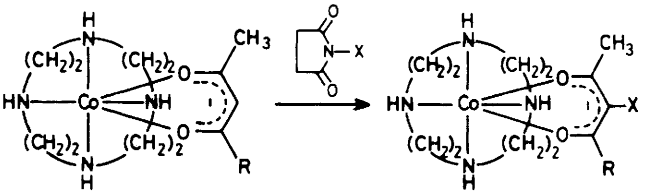
Synthesis, Characterization, and Crystal Structure Analysis of Pentane-2,4-dionato(1,4,7,10-tetra-azacyclododecane)cobalt(III) Diperchlorate Monohydrate and its Brominated Complex (3-Bromopentane-2,4-dionato)(1,4,7,10-tetra-azacyclododecane)-cobalt(III) Diperchlorate Hemihydrate †

Naohide Matsumoto,* Akira Hirano, Tadanori Hara, and Akira Ohyoshi
Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860, Japan

Pentane-2,4-dionato(1,4,7,10-tetra-azacyclododecane)cobalt(III) diperchlorate (1) reacts with *N*-bromosuccinimide to give its brominated complex, (3-bromopentane-2,4-dionato)(1,4,7,10-tetra-azacyclododecane)cobalt(III) diperchlorate (2). The complexes have been characterized by elemental analyses, electrical conductivity measurements, i.r., ^1H n.m.r., and electronic spectra. The three-dimentional *X*-ray crystallographic structure determination of the title complexes confirmed the completion of bromination at the 3-position of the pentane-2,4-dionato-moiety without altering the stereochemistry of the co-ordination sphere and macrocyclic ligand. The parent (1) crystallizes in the space group $Pna2_1$, with $a = 18.974(6)$, $b = 13.403(4)$, $c = 8.928(2)$ Å, and $Z = 4$, while complex (2) crystallizes in the space group *Pbca*, with $a = 15.138(4)$, $b = 21.360(5)$, $c = 14.066(7)$ Å, and $Z = 8$. The structures were solved by the heavy-atom method to give $R = 0.0499$ and 0.0635 for (1) and (2), respectively. The cobalt ion is co-ordinated in a distorted octahedral fashion with the four nitrogen atoms of the 12-membered macrocyclic ligand and two oxygen atoms of the pentane-2,4-dionato-moiety in a *cis* position, in which the distortion from the regular octahedron is found in the donor nitrogen atoms of the macrocyclic ligand. The six-membered chelate ring consisting of the 3-bromopentane-2,4-dionato group and the cobalt ion slightly deviates from the overall planarity, with deviations of 0.19 and 0.18 Å for the Co and Br atoms, while the planarity of the corresponding chelate ring of (1) is preserved within ±0.04 Å. The cation of (1) exhibits a mirror plane passing through the pentane-2,4-dionato-moiety, Co, and two nitrogen atoms in a *cis* position, while for the brominated complex (2) the symmetry is not preserved due to the deviation from overall planarity of the chelate ring.

Since Collman and co-workers[1,2] discovered the quasi-aromatic character of the chelate ring of a pentane-2,4-dionato–metal complex and the reactivity of the chelate ring towards electrophilic substitution reaction, electrophilic substitution reactions of pentane-2,4-dionato–metal complexes with various reagents such as *N*-halogenosuccinimides and acid chlorides have been carried out in order to introduce a substituent at the 3-position of the chelate ring.[3,4] Kuroda and co-workers[5-7] succeeded in the halogenation and nitration of some mixed-ligand pentane-2,4-dionatocobalt(III) complexes, $[CoA_4(pd)][ClO_4]_2$ [pd = pentane-2,4-dionate; $A_4 = (NH_3)_4$, $(H_2NCH_2CH_2NH_2)_2$, 3,6-diazaoctane-1,8-diamine, or tris(2-aminoethyl)amine].

We report herein the preparation and characterization of pentane-2,4-dionato(1,4,7,10-tetra-azacyclododecane)cobalt(III) diperchlorate (1) and its brominated complex (3-bromopentane-2,4-dionato)(1,4,7,10-tetra-azacyclododecane)cobalt(III) diperchlorate (2), where the 12-membered macrocyclic ligand (abbreviated as L) is known to form only a *cis* type of complex with a cobalt(III) ion.[8] The complexes have been characterized by elemental analyses, electrical conductivity measurements, i.r., ^1H n.m.r., and electronic spectra. The crystal structures of (1) and (2) have been determined by single-crystal *X*-ray diffraction in order to confirm the completion of bromination at the 3-position of the pentane-2,4-dionato-moiety (for reaction see Scheme) and to compare the molecular structure of the reactant with that of the product.



Scheme. Reaction scheme of $[CoL(pd)]^{2+}$ with *N*-halogenosuccinimide to give $[CoL(bpd)]^{2+}$ ($R = CH_3$, $X = Br$)

Experimental

Physical Measurements.—All chemicals used for the synthesis of the compounds were of reagent grade and were used without further purification. Elemental analysis was performed by Mr. S. Miyazaki at the Technical Service Center of Kumamoto University. Visible and ultraviolet spectra were obtained with a Hitachi recording spectrophotometer 323, while infrared spectra were recorded as KBr discs with a JASCO A-702. The 100-MHz ^1H n.m.r. spectra were recorded on a JEOL MH 100 spectrometer, using deuterium oxide as the solvent and $SiMe_4$ as the internal reference at room temperature. Conductivity measurements were performed with a Denki Kagaku AOC-10 instrument on *ca.* 10^{-3} mol dm^{-3} aqueous solutions at room temperature. The thermogravimetric analyses (t.g.a.) were carried out on a Shimadzu TGC-20 microthermobalance at the heating rate of 5 °C min^{-1} using *ca.* 20 mg of the sample for each run, according to the method in the literature.[9]

Synthesis.—1,4,7,10-Tetra-azacyclododecane tetrahydro-

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† *Supplementary data available* (No. SUP 23685, 43 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

chloride (L·4HCl) was prepared according to the high-yield synthetic procedure of Raymond and co-workers [10] applied for the preparation of 1,5,9,13-tetra-azacyclohexadecane. The tetratosylated tetra-amine, 1,3,6,8-tetrakis(toluene-*p*-sulphonyl)-3,6-diazaoctane-1,8-diamine [11] (0.3 mol, 230 g), was dissolved in *NN*-dimethylformamide (2 dm^3) and sodium hydride (50 g as a 50% suspension in oil) added in small portions to the solution. After the reaction was complete, the solution was filtered to remove excess sodium hydride. A solution of 1,2-bis(toluene-*p*-sulphonyloxy)ethane [12] (0.3 mol, 111 g) in *NN*-dimethylformamide (1 dm^3) was added dropwise to the solution at 110 °C with vigorous stirring. After the completion of addition, the mixture was refluxed for 6 h at 110 °C. The solution volume was then reduced to 800 cm^3 by evaporation. After the solution was cooled to room temperature, water (2.5 dm^3) was slowly added to precipitate a white solid. The resultant product was filtered off, washed with a large amount of water, and dried.

The tosylated macrocyclic compound, 1,4,7,10-tetrakis-(toluene-*p*-sulphonyl)-1,4,7,10-tetra-azacyclododecane (120 g), was refluxed in 97% sulphuric acid (400 cm^3) at *ca.* 100 °C for 48 h. The resultant dark solution was cooled in an ice-bath, and ethanol (1 dm^3) and then diethyl ether (1 dm^3) were slowly added to precipitate the product. The resultant precipitate was filtered off and washed several times with ethanol and ether. The solid was dissolved in water (400 cm^3) and the pH of the solution adjusted to 10 with sodium hydroxide. The solution was filtered to remove the sub-product and then the filtrate was extracted with chloroform (4 × 500 cm^3). The chloroform layer was separated and evaporated to the minimum volume. The crude product was dissolved in 20% hydrochloric acid (100 cm^3) in an ice-bath and the solution heated until the crystalline material began to precipitate. After the solution was left to stand in a refrigerator overnight the resulting white crystals were filtered off, washed with methanol and acetone, and dried (yield *ca.* 25 g, 39%).

Carbonato(1,4,7,10-tetra-azacyclododecane)cobalt(III) perchlorate, $[CoL(CO_3)]ClO_4$, was prepared according to the method of Collman and Schneider.[13]

Pentane-2,4-dionato(1,4,7,10-tetra-azacyclodecane)cobalt(III) Diperchlorate Monohydrate, $[CoL(pd)][ClO_4]_2{\cdot}H_2O$ (1), *and (3-Bromopentane-2,4-dionato)(1,4,7,10-tetra-azacyclododecane)cobalt(III) Diperchlorate Hemihydrate*, $[CoL(bpd)][ClO_4]_2{\cdot}0.5H_2O$ (2).—The method of the preparation for $[CoA_4\{CH_3COC(X)COCH_3\}][ClO_4]_2$ (X = Cl, Br, I, or NO_2; A_4 as before) by Yoshitani *et al.*[6] was applied for the syntheses of complexes (1) and (2). To a solution of $[CoL(CO_3)]ClO_4$ (2.5 g) in 2 mol dm^{-3} $HClO_4$ (8 cm^3) was added a solution of pentane-2,4-dione (1.5 cm^3) in 1 mol dm^{-3} sodium hydroxide (12 cm^3). The mixture was stirred at *ca.* 70 °C for several hours, during which time red crystals began to form. After the solution was left overnight at room temperature, well grown rhombic crystals were separated, filtered off, and washed with ethanol and ether (Found: C, 28.5; H, 5.45; N, 10.0. Calc. for $C_{13}H_{27}Cl_2CoN_4O_{10}{\cdot}H_2O$: C, 28.55; H, 5.35; N, 10.25%). ^1H N.m.r.: δ 2.16, 2.24 (d), 2.60—3.68 (m), and 5.86 (s).

To a solution of $[CoL(pd)][ClO_4]_2{\cdot}H_2O$ (1) (1.0 g) in water (10 cm^3) was added a solution of *N*-bromosuccinimide (0.5 g) in acetone (10 cm^3). The mixture was stirred at *ca.* 50 °C for 1 h and then evaporated to the minimum volume under reduced pressure. The resultant solid was dissolved in water (10 cm^3) and the solution filtered. After the addition of several drops of 6 mol dm^{-3} $HClO_4$, the solution was left overnight at room temperature to give well grown plate crystals (Found: C, 25.4; H, 4.7; N, 8.85. Calc. for $C_{13}H_{26}BrCl_2CoN_4O_{10}{\cdot}0.5H_2O$: C, 25.3; H, 4.4; N, 8.85%). ^1H N.m.r.: δ 2.50, 2.58 (d), and 2.66—3.64 (m).

Crystallographic Measurements.—Crystals of complexes (1) and (2) suitable for *X*-ray diffraction study were prepared by slow precipitation from their aqueous solutions at room temperature. The diffraction data were measured on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite-monochromatized Mo-K_α radiation at 20 ± 1 °C. The unit-cell parameters of each crystal were determined by least-squares refinement based on 20 reflections. Density was measured by the method of flotation in a mixture of chloroform and 1,3-dibromopropane.

The intensity data were collected using the θ—2θ scan technique at the scan rate of 8° min^{-1}. For weak reflections the peak scan was repeated up to three times depending on their intensities. Three reflections were monitored every 100 reflections throughout the set and displayed no decay of intensity. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. Reflection data with $|F_o| > 3\sigma(|F_o|)$ were considered ' observed ' and used in the refinement. The crystal data and experimental details are given in Table 1.

Structure solution and refinement. The structures were solved by the heavy-atom method and refined by the block-diagonal least-squares method. In the least-squares procedure, the function minimized was $\Sigma w||F_o| - k|F_c||^2$, where $w = 1/\sigma(|F_o|)^2$. Neutral-atom scattering factors were taken from ref. 14 for H, C, N, O, Cl, Br, and Co. Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for all the component atoms were also taken from the literature.[14] All calculations were carried out on a FACOM M-200 computer at the Computer Center of Kyushu University by the use of a local version [15] of the UNICS II [16] and the ORTEP programs.[17]

$[CoL(pd)][ClO_4]_2{\cdot}H_2O$ (1). Systematic absences (*0kl*, $k + l$ = odd; *h0l*, h = odd) indicated that the space group was either $Pna2_1$ or *Pnam*. The space group $Pna2_1$ was selected because the Wilson statistics suggested a non-centrosymmetric space group and the Patterson synthesis was explained only by assuming the space group $Pna2_1$. The cobalt atom position was determined from a three-dimensional Patterson synthesis and all the non-hydrogen atoms were located from subsequent Fourier and difference-Fourier syntheses. In the course of structure analysis, it became apparent that the oxygen atoms of one of the perchlorate ions were subjected to disorder. The occupancy factors were assigned to the possible positions located in the difference-Fourier map according to the peak heights. Refinement was carried out by using initially isotropic thermal parameters and then anisotropic ones. Hydrogen atoms were inserted at the calculated positions and the final refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0499$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.0399$. The final difference-Fourier synthesis showed no remaining regions of electron density, peaks being less than 0.4 e Å^{-3}.

$[CoL(bpd)][ClO_4]_2{\cdot}0.5H_2O$ (2). The Br and Co atom positions were determined from a three-dimensional Patterson synthesis. Subsequent Fourier and difference-Fourier syntheses revealed all the non-hydrogen atoms except for the water molecule of crystallization. Refinement was carried out initially by isotropic thermal parameters and then anisotropic ones. At this stage, a difference-Fourier synthesis was calculated and located an oxygen atom of the water as a crystal solvent and almost all of the hydrogen atoms. An occupancy factor of 0.5 was adopted for the water, considering the peak height and the adjustment of the thermal analysis. After including the oxygen atom in the refinement, a difference-Fourier synthesis was calculated and located the hydrogen atoms. Further refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydro-

Table 1. Crystal data for $[CoL(pd)][ClO_4]_2 \cdot H_2O$ (1) and $[CoL(bpd)][ClO_4]_2 \cdot 0.5H_2O$ (2)

Complex	(1)	(2)
Formula	$C_{13}H_{29}Cl_2CoN_4O_{11}$	$C_{13}H_{27}BrCl_2CoN_4O_{10.5}$
M	547.2	617.1
Space group	$Pna2_1$	$Pbca$
a/Å	18.974(6)	15.138(4)
b/Å	13.403(4)	21.360(5)
c/Å	8.928(2)	14.066(7)
U/Å^3	2 270.4	4 548.4
D_m/g cm^{-3}	1.59	1.80
D_c/g cm^{-3}	1.600	1.802
Z	4	8
F(000)	1 136	2 504
λ(Mo-K_α)/Å	0.710 73	0.710 73
μ(Mo-K_α)/cm^{-1}	10.8	29.9
Crystal size/mm	0.2 × 0.3 × 0.5	0.4 × 0.4 × 0.3
$2\theta_{max.}$/°	52.0	44.5
No. of unique reflections $[F_o > 3\sigma(F_o)]$	1 596	2 074

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for $[CoL(pd)][ClO_4]_2 \cdot H_2O$ (1) and $[CoL(bpd)][ClO_4]_2 \cdot 0.5H_2O$ (2)

	(1)				(2)		
Atom	x	y	z	Atom	x	y	z
Co	1 325(0)	1 936(1)	0	Br	1 443(1)	3 583(1)	−619(1)
O(1)	1 115(2)	567(3)	83(22)	Co	2 237(1)	1 329(1)	200(1)
O(2)	2 308(2)	1 706(4)	38(22)	O(1)	1 476(4)	1 687(3)	−722(5)
N(1)	1 211(4)	2 108(6)	2 183(9)	O(2)	2 296(4)	2 080(3)	881(5)
N(2)	318(3)	2 085(4)	−2(25)	N(1)	3 312(5)	1 469(4)	−554(6)
N(3)	1 302(4)	2 059(5)	−2 185(8)	N(2)	2 084(5)	578(4)	−571(6)
N(4)	1 556(3)	3 338(4)	10(24)	N(3)	1 282(5)	974(4)	992(6)
C(1)	550(5)	1 961(7)	2 595(12)	N(4)	3 021(5)	995(4)	1 169(6)
C(2)	39(5)	2 438(7)	1 495(11)	C(1)	3 297(7)	1 030(6)	−1 359(8)
C(3)	102(5)	2 576(8)	−1 365(12)	C(2)	2 940(7)	421(5)	−1 016(7)
C(4)	463(5)	1 982(8)	−2 566(12)	C(3)	1 606(7)	97(5)	−7(8)
C(5)	1 567(6)	3 062(9)	−2 622(13)	C(4)	878(7)	450(5)	457(7)
C(6)	1 933(5)	3 542(7)	−1 284(14)	C(5)	1 658(7)	765(5)	1 930(8)
C(7)	1 942(5)	3 538(7)	1 523(13)	C(6)	2 548(7)	1 049(5)	2 094(7)
C(8)	1 499(6)	3 097(7)	2 639(11)	C(7)	3 858(7)	1 360(5)	1 082(8)
C(9)	1 564(4)	−141(5)	39(30)	C(8)	4 141(7)	1 357(6)	87(8)
C(10)	2 279(4)	−31(6)	66(33)	C(9)	1 340(6)	2 275(5)	−872(7)
C(11)	2 608(4)	870(6)	86(26)	C(10)	1 649(6)	2 739(5)	−281(7)
C(12)	1 225(5)	−1 159(6)	151(37)	C(11)	2 087(6)	2 627(5)	583(7)
C(13)	3 393(4)	921(7)	74(37)	C(12)	769(8)	2 393(6)	−1 705(8)
Cl(1)	513(1)	5 747(2)	34(10)	C(13)	2 333(8)	3 144(5)	1 256(8)
Cl(2)	3 767(1)	4 687(1)	−40(10)	Cl(1)	−781(2)	1 947(1)	1 082(2)
O(PA) [a]	364(7)	4 815(9)	−429(40)	Cl(2)	752(2)	369(1)	−3 014(2)
O(PB) [a]	848(8)	6 508(9)	−686(27)	O(3)	−918(7)	2 113(5)	161(7)
O(PC) [a]	625(8)	5 077(11)	1 154(19)	O(4)	92(6)	2 094(5)	1 259(8)
O(PD) [a]	937(9)	6 079(12)	1 149(18)	O(5)	−1 339(6)	2 318(4)	1 667(6)
O(PE) [a]	875(9)	5 525(15)	−1 318(22)	O(6)	−898(7)	1 317(4)	1 199(9)
O(PF) [b]	−175(4)	6 119(7)	−8(37)	C(7)	783(10)	108(6)	−2 161(8)
O(7)	3 555(6)	4 898(9)	1 393(12)	C(8)	489(6)	990(4)	−3 005(7)
O(8)	3 357(5)	5 255(7)	−1 012(13)	O(9)	1 539(8)	310(5)	−3 424(13)
O(9)	3 629(3)	3 686(5)	131(30)	O(10)	209(10)	14(6)	−3 492(12)
O(10)	4 474(3)	4 906(5)	−198(29)	O(H_2O) [c]	714(12)	−1 005(7)	1 243(11)
O(H_2O)	2 605(4)	1 648(6)	4 433(23)				

[a] Occupancy factor 0.64. [b] Occupancy factor 0.80. [c] Occupancy factor 0.5.

gen atoms gave $R = 0.0635$ and $R' = 0.0550$. The final difference-Fourier synthesis showed no remaining regions of electron density, peaks being less than 0.5 e Å^{-3}.

Final positional parameters with their estimated standard deviations are given in Table 2.

Results and Discussion

The parent complex $[CoL(pd)][ClO_4]_2$ (1) reacts electrophilically with *N*-bromosuccinimide to produce its brominated complex $[CoL(bpd)][ClO_4]_2$ (2). Thermogravimetric analysis (t.g.a.) indicated that complexes (1) and (2) crystallize as the monohydrate and the hemihydrate, respectively, where the thermal process has a weight loss corresponding to the quantitative water molecule estimated by the elemental analyses, and the weight change was observed at 40—120 °C. Molar electrical conductivities measured in water were 199 and 194 S cm^2 mol^{-1} for (1) and (2), respectively; these values are in the expected range for 1 : 2 electrolytes.[18]

The infrared spectrum of the parent complex (1) showed

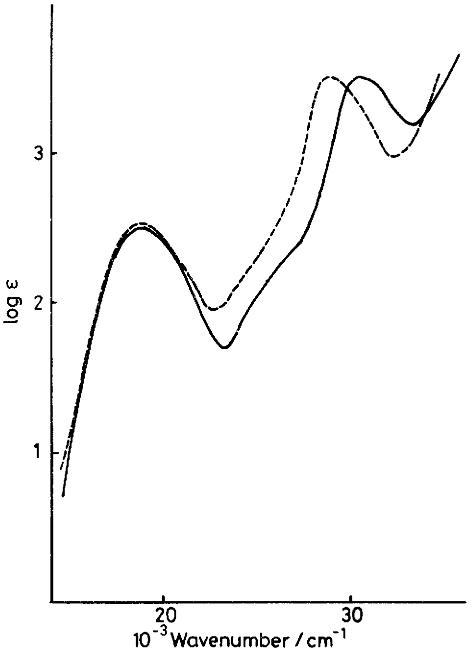

Figure 1. Absorption spectra (ε in dm^3 mol^{-1} cm^{-1}) of [CoL(pd)][ClO_4]$_2$·H_2O (1) (——) and [CoL(bpd)][ClO_4]$_2$·0.5H_2O (2) (– – – –)

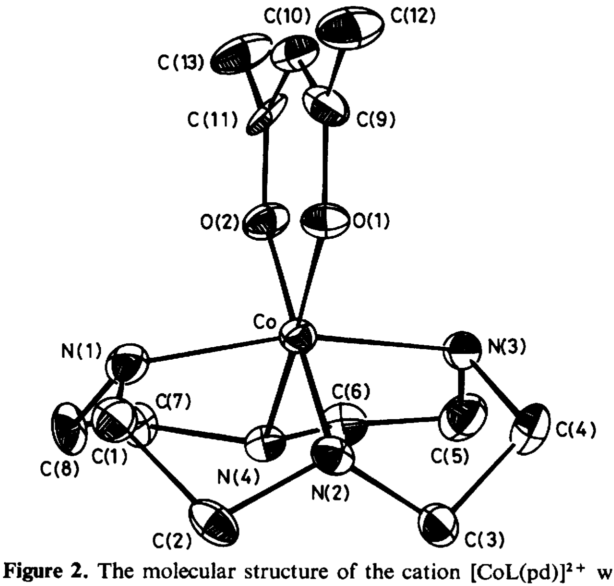

Figure 2. The molecular structure of the cation [CoL(pd)]$^{2+}$ with the atom-numbering scheme used

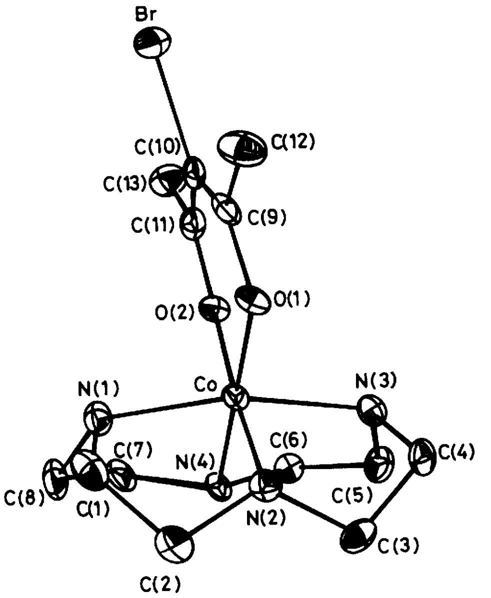

Figure 3. The molecular structure of the cation [CoL(bpd)]$^{2+}$ with the atom-numbering scheme used

two intense bands at 1 525 and 1 575 cm^{-1} in the region 1 500—1 600 cm^{-1} which can be assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$, respectively,[19] while that of (2) showed only a band at 1 555 cm^{-1} in this region.

The ^{1}H n.m.r. spectra were measured in deuterium oxide and $SiMe_4$ was used as the internal reference. The ^{1}H n.m.r. spectrum of the parent complex (1) consists of a doublet (methyl), multiplet (methylene), and singlet (methine) from the high-field region. The resonance of the methine proton at the 3-position of the pentane-2,4-dionato-moiety (5.86 p.p.m.) disappeared in that of the brominated complex (2), supporting the introduction of the substituent at this position. The doublet with an averaged chemical shift of 2.20 p.p.m. for the parent complex (1) shifts to lower field (2.54 p.p.m.) upon bromination. This shift was also observed in the related system of the complexes [Co{$CH_3COC(X)COCH_3$}$_3$] and [CoA_4{$CH_3COC(X)COCH_3$}]$^{2+}$, in which the halogenation (X = Cl, Br, or I) and nitration (X = NO_2) have been well established,[5] being indicative of the substitution.

The absorption spectra of (1) and (2) are shown in Figure 1. The spectral pattern is quite similar to the related low-spin six-co-ordinate cobalt(III) complexes, [Co{$CH_3COC(X)COCH_3$}$_3$] and [CoA_4{$CH_3COC(X)COCH_3$}]$^{2+}$ (X = H, Cl, Br, I, or NO_2).[5] The spectra exhibit two bands (first band at *ca.* 2.0 × 10^4 cm^{-1} and second bands as a shoulder at 2.7 × 10^4 cm^{-1}) with absorption coefficients of *ca.* 200 and 150 dm^3 mol^{-1} cm^{-1} respectively, which are attributable to *d–d* transitions.[20–22]

The spectra also exhibit a specific band with an absorption coefficient of *ca.* 4 000 dm^3 mol^{-1} cm^{-1}, which can be attributed to the charge-transfer band from the metal t_{2g} to the ligand π^* orbital.[23] As shown in Figure 1, the specific band shifts to lower wavenumber with equal intensity upon bromination, while the *d–d* transition bands show no shift upon bromination.

Crystal and Molecular Structures of (1) *and* (2).—The perspective drawings of the cations [CoL(pd)]$^{2+}$ of (1) and [CoL(bpd)]$^{2+}$ of (2) with the atom-numbering scheme used [corresponding atoms in (1) and (2) are given the same number] are shown in Figures 2 and 3, respectively. Details of bond distances and angles with estimated standard deviations are given in Table 3. As shown in Figures 2 and 3 and Table 3, the molecular conformation and dimensions of (1) are quite similar to those of (2). Any further description is now exemplified by the parent complex (1), unless any significant difference between them is noted. The *X*-ray analyses of (1) and (2) confirmed the completion of bromination at the 3-position of the pentane-2,4-dionato-moiety without altering the stereochemistry of the co-ordination sphere and macrocyclic ligand. The cation moiety of (1) exhibits nearly exactly a mirror plane passing through the pentane-2,4-dionato-moiety, cobalt ion, N(2), and N(4) atoms, although the mirror symmetry is not required crystallographically. For the complex

Table 3. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $[CoL(pd)][ClO_4]_2 \cdot H_2O$ (1) and $[CoL(bpd)][ClO_4]_2 \cdot 0.5H_2O$ (2)

	(1)	(2)
Co–O(1)	1.878(4)	1.894(6)
Co–O(2)	1.890(4)	1.870(6)
Co–N(1)	1.974(8)	1.964(8)
Co–N(2)	1.921(5)	1.951(8)
Co–N(3)	1.958(7)	1.976(7)
Co–N(4)	1.929(5)	1.943(7)
O(1)–C(9)	1.275(8)	1.289(11)
O(2)–C(11)	1.259(9)	1.280(11)
N(1)–C(1)	1.322(12)	1.470(14)
N(1)–C(8)	1.489(12)	1.563(13)
N(2)–C(2)	1.512(22)	1.477(13)
N(2)–C(3)	1.442(22)	1.484(13)
N(3)–C(4)	1.630(12)	1.479(13)
N(3)–C(5)	1.487(13)	1.505(13)
N(4)–C(6)	1.386(21)	1.490(12)
N(4)–C(7)	1.560(21)	1.493(12)
C(1)–C(2)	1.520(13)	1.489(15)
C(3)–C(4)	1.500(14)	1.486(15)
C(5)–C(6)	1.523(16)	1.495(15)
C(7)–C(8)	1.431(14)	1.464(15)
C(9)–C(10)	1.364(10)	1.375(13)
C(9)–C(12)	1.511(11)	1.478(15)
C(10)–C(11)	1.359(10)	1.405(14)
C(11)–C(13)	1.491(11)	1.500(15)
Br–C(10)	—	1.890(9)
Cl(1)–O(PA)	1.345(15)	—
Cl(1)–O(PB)	1.362(16)	—
Cl(1)–O(PC)	1.360(17)	—
Cl(1)–O(PD)	1.354(17)	—
Cl(1)–O(PE)	1.420(20)	—
Cl(1)–O(PF)	1.397(8)	—
Cl(1)–O(3)	—	1.359(10)
Cl(1)–O(4)	—	1.380(9)
Cl(1)–O(5)	—	1.421(8)
Cl(1)–O(6)	—	1.368(9)
Cl(2)–O(7)	1.380(13)	1.323(11)
Cl(2)–O(8)	1.391(11)	1.384(8)
Cl(2)–O(9)	1.375(7)	1.329(14)
Cl(2)–O(10)	1.380(7)	1.304(14)

	(1)	(2)
O(1)–Co–O(2)	92.8(2)	91.8(2)
O(1)–Co–N(1)	93.0(6)	94.1(3)
O(1)–Co–N(2)	83.7(2)	83.0(3)
O(1)–Co–N(3)	96.7(6)	95.4(3)
O(1)–Co–N(4)	177.3(8)	177.7(3)
O(2)–Co–N(1)	96.2(6)	96.1(3)
O(2)–Co–N(2)	176.4(3)	174.8(3)
O(2)–Co–N(3)	93.0(6)	94.3(3)
O(2)–Co–N(4)	86.2(2)	85.8(3)
N(1)–Co–N(2)	83.1(7)	85.6(3)
N(1)–Co–N(3)	166.1(3)	165.4(3)
N(1)–Co–N(4)	84.6(6)	85.8(3)
N(2)–Co–N(3)	88.1(7)	84.8(3)
N(2)–Co–N(4)	97.1(2)	99.1(3)
N(3)–Co–N(4)	85.8(6)	84.8(3)
Co–O(1)–C(9)	125.7(4)	126.9(6)
Co–O(2)–C(11)	126.3(4)	127.0(6)
Co–N(1)–C(1)	111.1(6)	107.8(6)
Co–N(1)–C(8)	109.4(5)	109.3(5)
C(1)–N(1)–C(8)	113.8(7)	111.0(7)
Co–N(2)–C(2)	112.3(10)	108.5(6)
Co–N(2)–C(3)	109.2(9)	109.2(6)
C(2)–N(2)–C(3)	120.2(6)	119.7(7)
Co–N(3)–C(4)	102.9(5)	107.8(5)
Co–N(3)–C(5)	109.2(6)	109.3(5)
C(4)–N(3)–C(5)	109.3(7)	112.1(7)
Co–N(4)–C(6)	107.7(9)	106.9(5)
Co–N(4)–C(7)	106.1(8)	105.5(6)
C(6)–N(4)–C(7)	116.3(6)	115.9(7)
N(1)–C(1)–C(2)	111.3(8)	108.2(8)
N(1)–C(8)–C(7)	113.1(8)	108.3(8)
N(2)–C(2)–C(1)	102.4(7)	104.8(8)
N(2)–C(3)–C(4)	103.3(8)	104.1(8)
N(3)–C(4)–C(3)	105.2(7)	107.5(8)
N(3)–C(5)–C(6)	109.2(8)	110.9(8)
N(4)–C(6)–C(5)	109.5(9)	105.4(7)
N(4)–C(7)–C(8)	104.7(8)	108.3(8)
O(1)–C(9)–C(10)	125.6(6)	123.2(8)
O(1)–C(9)–C(12)	112.6(6)	112.9(8)
C(10)–C(9)–C(12)	121.3(7)	123.6(9)
C(9)–C(10)–C(11)	123.5(7)	124.1(9)
O(2)–C(11)–C(10)	125.6(7)	123.6(9)
O(2)–C(11)–C(13)	114.2(6)	113.7(8)
C(10)–C(11)–C(13)	119.9(7)	122.5(9)
Br–C(10)–C(9)	—	118.6(7)
Br–C(10)–C(11)	—	117.1(7)

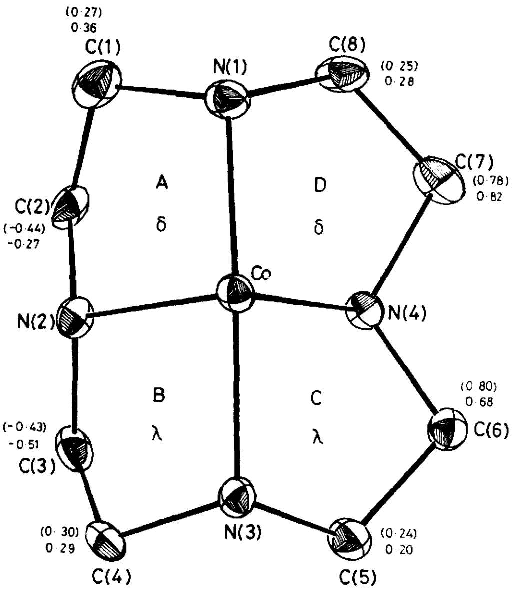

Figure 4. The chelate ring conformations in L assigned for arbitrary absolute configurations. The distances (Å) of the two carbon atoms in the CoN_2C_2 chelate ring from the CoN_2 mean plane are given for (1) and for (2) (in parentheses)

(1), the overall planarity of the six-membered chelate ring consisting of the pentane-2,4-dionato-moiety and the cobalt ion is preserved within ±0.04 Å of the deviations of the component atoms. On the other hand, the corresponding chelate ring of (2) slightly deviates from the overall planarity with deviations of 0.19, 0.18, −0.12, and −0.10 Å for the Co, Br, C(12), and C(13) atoms, respectively. The torsion angles of 6.9° [C(12)–C(9)–C(10)–Br] and −4.2° [C(13)–C(11)–C(10)–Br] are also indicative of the deviation from the planarity of the chelate ring.

The co-ordination geometry around the cobalt ion is a distorted octahedron, where four nitrogen atoms of the macrocyclic ligand and two oxygen atoms of pentane-2,4-dionato-moiety are co-ordinated to the cobalt ion in a *cis* position. The distorsion from a regular octahedron is found in the nitrogen

Table 4. Possible hydrogen bond distances (Å) of [CoL(pd)]-$[ClO_4]_2 \cdot H_2O$ (1) and [CoL(bpd)]$[ClO_4]_2 \cdot 0.5H_2O$ (2)

(*a*) [CoL(pd)]$[ClO_4]_2 \cdot H_2O$

		symmetry code *
N(1)–O(8)	3.07	$-x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$
N(2)–O(10)	3.11	$x - \frac{1}{2}, -y + \frac{1}{2}, z$
N(3)–O(7)	3.17	$-x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$
N(4)–O(PA)	3.03	x, y, z
N(4)–O(PC)	3.09	x, y, z

(*b*) [CoL(bpd)]$[ClO_4]_2 \cdot 0.5H_2O$

		symmetry code *
N(1)–O(5)	3.07	$x + \frac{1}{2}, -y + \frac{1}{2}, -z$
N(2)–O(7)	3.14	x, y, z
N(3)–O(4)	3.01	x, y, z
N(4)–O(9)	2.92	$-x + \frac{1}{2}, -y, z + \frac{1}{2}$

* Symmetry operation was applied to second atom.

atoms of the 12-membered macrocyclic ligand. The angles N(1)–Co–N(3) [166.1(3)° in (1)] and N(2)–Co–N(4) [97.1(2)° in (1)] indicate that the ligand is too small to form a regular octahedron with the cobalt(III) ion, even in the *cis* complex. It is well known that the ligand L forms only *cis* complexes with cobalt(III) ions.[13]

Four five-membered chelate rings of the 12-membered macrocyclic ligand are shown in Figure 4. Two rings (A and B) are enantiomeric to each other, having an unsymmetric *gauche* conformation with δ and λ chiralities, while the other two rings (C and D) are also reflectionally related, having an unsymmetric envelope conformation with λ and δ chiralities, where the conformations are assigned as arbitrary absolute configurations. The configuration of the macrocyclic ligand can be also expressed by two asymmetrical atoms N(2) and N(4), and the combination of their chiralities is either *SS* or *RR*. So far two cobalt(III) complexes with the ligand L, [CoL-$(NO_2)_2$]Cl [24] and [CoL(CO_3)]$ClO_4 \cdot H_2O$,[25] have been subjected to single-crystal *X*-ray analysis and their macrocyclic configurations are the same as that of the present complexes. The methyl resonance of the pentane-2,4-dionato-moiety in the ^{1}H n.m.r. spectra appeared as a doublet. This splitting can be attributed to the difference of the neighbouring environment of the two methyl groups, *i.e.*, the conformational difference between (A, B) and (C, D) (Figure 4).

The macrocyclic conformation influences the Co–N bond distances. The Co–N(2) and Co–N(4) bond distances in (1) [1.921(5), 1.929(5) Å] are considerably shorter than Co–N(1) and Co–N(3) [1.974(8), 1.958(7) Å], presumably serving to diminish the angular strain at the N(1) and N(3) atoms. This feature is also observed in compound (2).

Possible hydrogen bond distances are given in Table 4. The nitrogen atoms of L of the complexes are hydrogen-bonded to the oxygen atoms of the perchlorate ions.

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