X-Ray Structural Studies of Green and Brown Crystals of *trans*-[$CoCl_2(N_48)$]X (N_48=1,4,7,10-Tetraazacyclopentadecane, X=NO_3^-, BF_4^-, and ClO_4^-)

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Crystal structures of green (X=NO_3^-(**1**), BF_4^-(**2**)) and brown (X=BF_4^-(**3**) and ClO_4^-(**4**)) salts of *trans*-[$CoCl_2(N_48)$]X (N_48=1,4,7,10-tetraazacyclopentadecane) were determined by an X-ray diffraction method. The complex cation is a *RSSR*(*SRRS*) isomer for the four chiral nitrogen atoms and has approximate C_2 symmetry. Green crystals **1** and **2** are monoclinic and have the chiral space group $P2_1$, comprising one antipode of the complex ion by spontaneous resolution, whereas brown crystals **3** and **4** are orthorhombic and a racemate. The eight-membered chelate ring formed by the N_48 ligand and the Co atom takes a distorted boat-boat (BB) form in **1** and **2**, whereas the conformation is disordered in **3** and **4** with BB (40%) and distorted twist-boat-chair (TBC; 60%) forms at room temperature. At 113 K, the eight-membered chelate ring in **4** takes exclusively the TBC form. The crystal data are as follows: [$CoCl_2(C_{11}H_{26}N_4)$]X, monoclinic NO_3 salt, **1**, $P2_1$, a=9.672(3), b=12.285(5), c=7.051(2) Å, β=94.70(3)°, V=835.0(5) Å^3, Z=2, T=300(1) K, final R=0.037 for 2381 reflections. Monoclinic BF_4 salt, **2**, $P2_1$, a=9.857(2), b=12.694(2), c=7.065(1) Å, β=94.34(2)°, V=881.5(2) Å^3, Z=2, T=300(1) K, final R=0.031 for 1880 reflections. Orthorhombic BF_4 salt, **3**, *Pcab*, a=12.816(1), b=22.359(2), c=12.388(1) Å, V=3549.8(5) Å^3, Z=8, T=300(1) K, final R=0.095 for 2086 reflections. Orthorhombic ClO_4 salt at 300(1) K, **4a**, *Pcab*, a=12.829(1), b=22.376(2), c=12.425(1) Å, V=3566.7(6) Å^3, Z=8, final R=0.070 for 1764 reflections; orthorhombic ClO_4 salt at 113(2) K, **4b**, a=12.630(2), b=22.276(5), c=12.354(2) Å, V=3475.7(11) Å^3, final R=0.109 for 2215 reflections.

During our study of 1,4,7,10-tetraazacycloalkane cobalt(III) complexes,[1] we found that *trans*-[$CoCl_2$-(N_48)]X (N_48=1,4,7,10-tetraazacyclopentadecane), in which the complex ion is a racemate with RSSR and SRRS configurations for the four chiral nitrogen atoms and has approximate C_2 symmetry, crystallizes in different colors; the BF_4^- and ClO_4^- salts form green and brown crystals, while the NO_3^- salt only green ones. The green crystals turn blue-green and the brown ones yellow-green at liquid nitrogen temperature, but in solution all of these crystals show the same ^{13}C NMR and electronic spectra.

To examine molecular structures of these crystals, X-ray structure analyses of the green NO_3^- (**1**), the green BF_4^-(**2**), the brown BF_4^-(**3**) and the brown ClO_4^-(**4a**) salts, and the brown ClO_4^- salt at 113 K (**4b**) have been carried out. The paper also reports electronic spectra in the solid state of the green BF_4^- and brown ClO_4^- salts at 303 and 113 K.

Experimental

Green crystals of **1** (monoclinic) were grown by slow evaporation of a methanol solution of the complex chloride[1] containing a few drops of 60% nitric acid. Green and brown crystals of **2** (monoclinic) and **3** (orthorhombic), respectively, and brown crystals of **4** (orthorhombic) were grown by keeping nitromethane solutions of the respective complex salts[1] and diethyl ether in a desiccator. Two types of crystals grow simultaneously, but can be easily distinguished by their crystal habit. Monoclinic crystals are prisms surrounded by {100}, {010}, {001}, and {01$\bar{1}$} planes. Orthorhombic ones are bipyramids with forms {111}.

Experimental conditions and refinement information are listed in Table 1. Intensities were measured on a Rigaku AFC-5 four circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å) up to 2θ=55° (2θ=60° for **1**). The ω scan technique was employed for orthorhombic crystals because of the broad peak profile. Data collection of **4b** at 113 K was carried out in a stream of cold nitrogen gas. Systematic absences of the monoclinic modification suggested the space group $P2_1$ or $P2_1/m$. Since Z=2 and the complex cation can neither lie on the special positions with site symmetry m nor those with i, the space group was deduced to be $P2_1$. Lattice constants were obtained from 18—25 2θ values (20°<2θ<30°).

The structures were solved by the Patterson-Fourier method. The function $\sum w(|F_o|-|F_c|)^2$ was minimized by block-diagonal least-squares refinement with weight $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$. Complex neutral-atom scattering factors were used.[2] The calculations for **1** were carried out on a HITAC M-680H computer at the Computer Center of Institute for Molecular Science and those of other complexes were performed on a FACOM M-380R computer at Keio University with the program system UNICS III.[3] The final atomic parameters are listed in Table 2.[4] All the hydrogen atoms in **2** and 21 of 26 hydrogen atoms in **1** were found on the different synthesis. The structural chirality was determined by the anomalous-scattering technique. For **3** and **4**, more than two possible positions were recognized for the C(8), C(9), and C(10) atoms of the eight-membered chelate ring. Thus the split atom model was adopted to construct several possible forms of the carbon chain. Because there were ambiguity which atoms are bonded or not, it was difficult to create the model structure. The populations of the atoms were estimated with the condition that the isotropic thermal parameters should be nearly equal

to each other. The number of hydrogen atoms found on difference synthesis was 19 and 13 among 26 for **3** and **4a**, respectively. The hydrogen atoms bonded to the carbon atoms in the eight-membered chelate ring were not taken into account because of the disordered structure. Anisotropic thermal parameters were introduced for all the non-hydrogen atoms except for the B atom of **3** and C(9B) and C(11) atoms of **4b**. The proposed split atom model seems to represent the disordered structure adequately although small residual electron densities remained on the difference maps. Bond distances and angles in the disordered carbon chain were 1.18(5)—1.79(7) Å and 93(2)—142(3)°.

Electronic Spectra in the solid state were obtained on a HITACHI U-3400 spectrometer. A nujol mull sample was coated on a quartz glass plate, and the plate was covered with a polyethylene film. The diffuse transmission light passed through the sample was collected on a integrating sphere and detected. Measurements at 113 K were carried out with a stream of cold nitrogen, and the temperature was monitored by a Cu-constantan thermocouple.

Results and Discussion

Crystal data show that the green and brown crystals are monoclinic and orthorhombic modifications, respectively, irrespective of the counter anions NO_3^-,

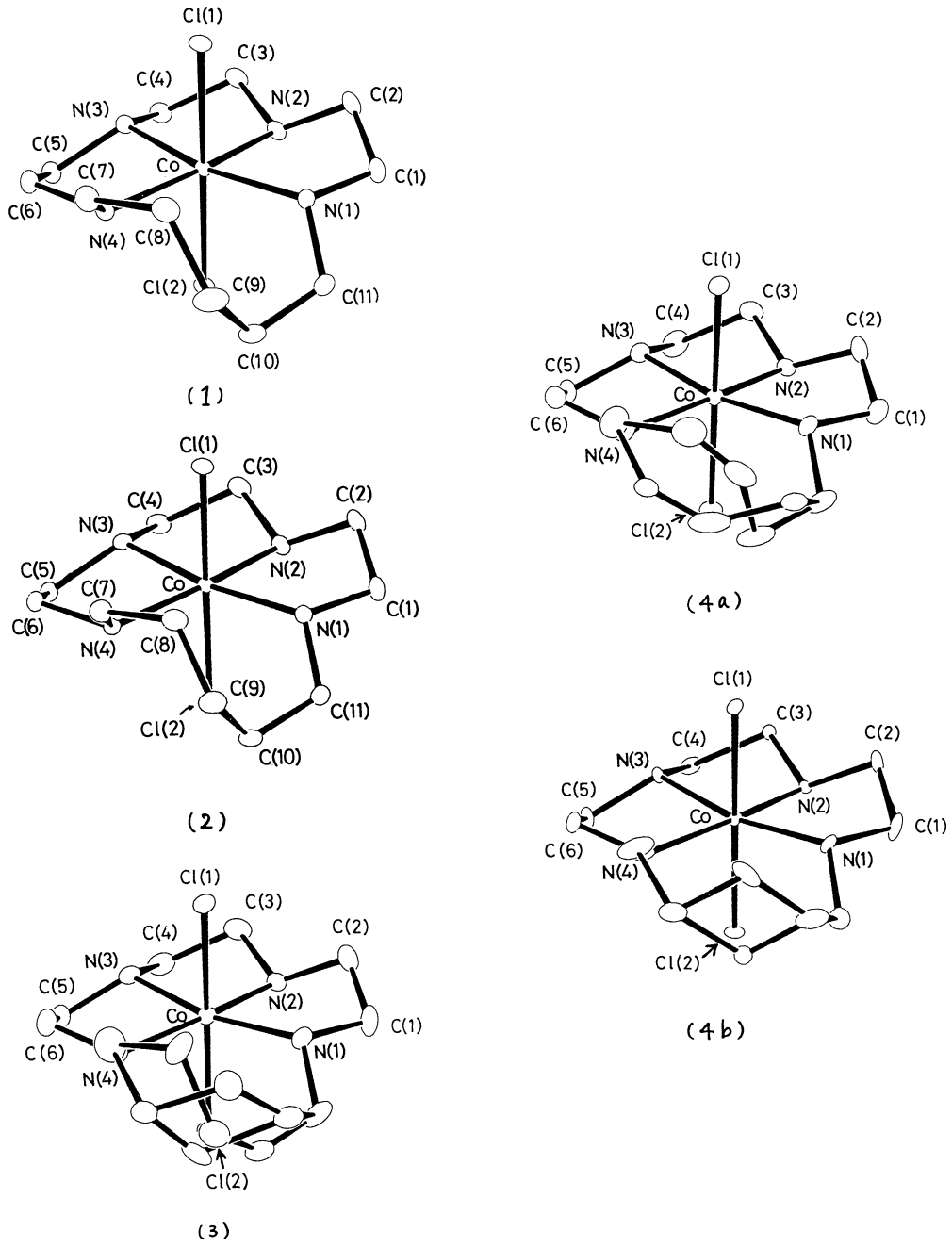

Fig. 1. ORTEP drawings[5] with 10% probability ellipsoids. In **3** and **4** the conformation of the eight-membered chelate ring is disordered. The numberings of disordered atoms are given in Fig. 2.

BF_4^-, and ClO_4^- (Table 1). Perspective views of the complexes in **1**—**4**, and the side views of the eight-membered chelate ring are presented in Figs. 1 and 2, respectively. The bond lengths and bond angles in the complex cation are listed in Table 3. Table 4 lists the hydrogen bonds. They are formed exclusively between the four-ligating nitrogen atoms of the complex cations and the oxygen or fluorine atoms of the counter anions. Complex cations and anions are held together by these hydrogen bonds. In all crystals, the complex cations have a RSSR(SRRS) configuration for the four nitrogen atoms of the N_48 ligand. The conformation of the eight-membered chelate rings, however, differs noticeably, reflecting the flexibility of the eight-membered chelte ring. Green crystals **1** and **2** have the chiral space group and comprise one antipode of the complex ion, whereas brown crystals **3** and **4** are a racemate. The structural chiralities of the crystals of **1** and **2** used for X-ray work happened to be the same (SRRS). The atomic parameters of **3** and **4** in Table 2 were selected to represent the asymmetric nitrogen atoms, SRRS for convenience of comparison with **1** and **2**. The five-membered chelate rings involving N(1)–C(1)–C(2)–N(2) and N(3)–C(5)–C(6)–N(4) moieties take a distorted envelope conformation, while that involving the N(2)–C(3)–C(4)–N(3) moiety a gauche one. The chelate angle of N(1)–Co–N(4) for the eight-membered chelate ring is from 104.0(1) to 107.2(3)°. The Co–N(1) and Co–N(4) bond lengths are 2.017(3)—2.048(8) Å, which is longer by ca. 0.1 Å than

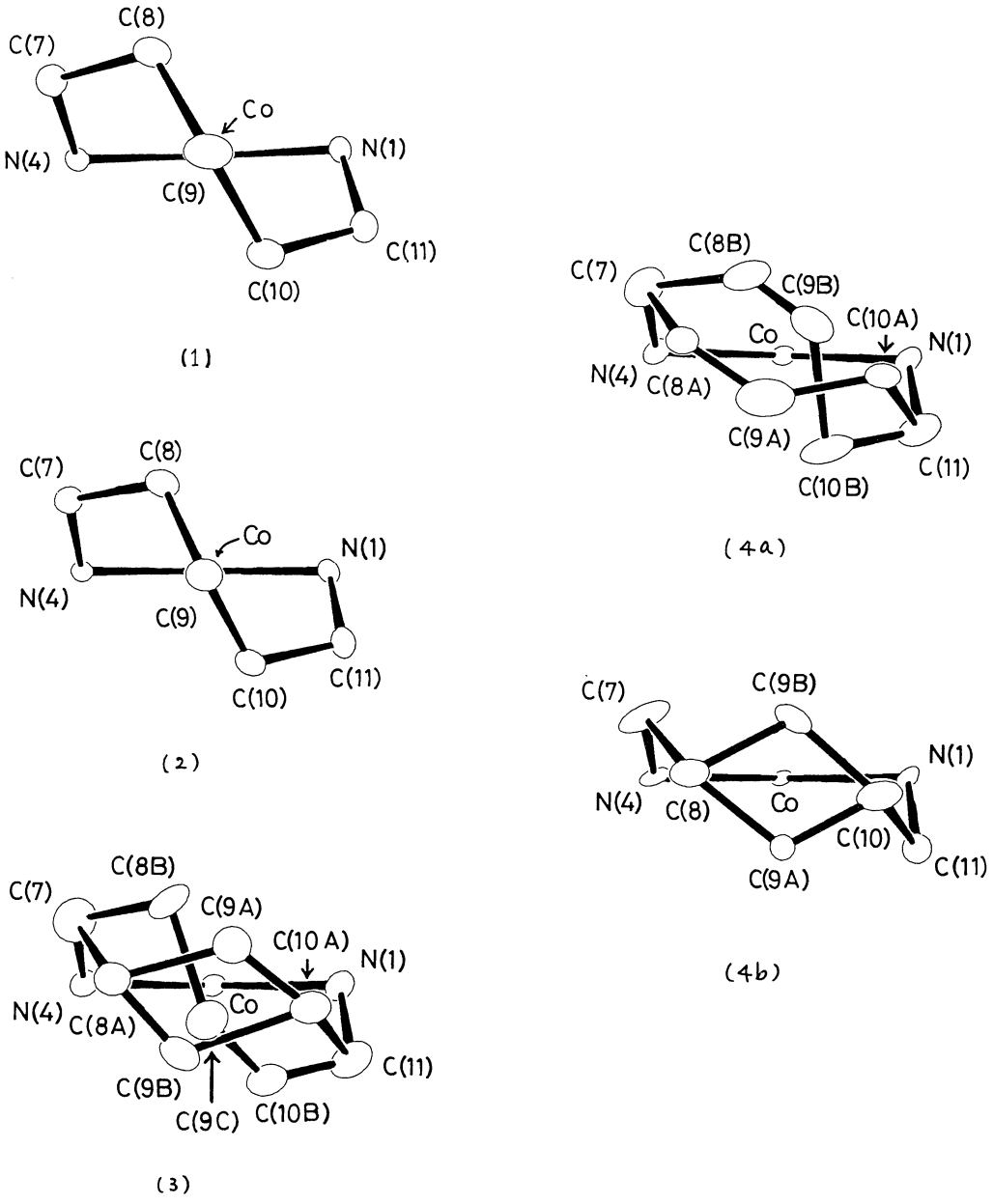

Fig. 2. Side views of the eight-membered chelate rings.

Table 1. Experimental Conditions and Details of Refinement for $[CoCl_2(C_{11}H_{28}N_4)]X$

	1	2	3	4a	4b
Counter ion, X^-	NO_3^-	BF_4^-	BF_4^-	ClO_4^-	ClO_4^-
Modification	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Temperature/K	300(1)	300(1)	300(1)	300(1)	113(2)
Formula weight	406.2	431.0	431.0	443.6	443.6
Observed density/Mg m^{-3}	1.619	1.615	1.638	1.655	
Calculated density/Mg m^{-3}	1.62	1.62	1.61	1.65	1.70
μ(Mo Kα)/mm^{-1}	1.37	1.32	1.31	1.44	1.47
Color and habit of crystal	Green prismatic	Green prismatic	Brown bipyramidal	Brown prismatic	Brown prismatic
Size of specimen/mm^3	0.55×0.28×0.15	0.33×0.28×0.35	0.30×0.33×0.35	0.20×0.17×0.17	0.20×0.17×0.17
Range of indices	h: −12→12; k: 0→15; l: 0→10	h: −12→12; k: 0→16; l: 0→9	h: 0→16; k: 0→29; l: −16→16	h: −16→16; k: 0→29; l: 0→16	h: −16→16; k: 0→28; l: 0→16
Number of standard reflections	3	5	4	3	3
and their variation	0.99—1.00	0.99—1.00	0.98—1.00	0.91—1.00	0.99—1.01
Number of reflections measured	2591	2280	7958	8012	7801
Number of reflections observed $[\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)]$	2381	2010	3658	3062	3777
R	0.037	0.031	0.095	0.070	0.109
wR	0.039	0.038	0.097	0.068	0.089
S	0.69	1.4	2.8	1.8	1.9
R'[a]	0.040	0.034			
Number of observed unique reflections	2381	1880	2086	1764	1562
Transmission factor		0.646—0.720	0.688—0.714	0.732—0.821	0.727—0.817

a) Refinement with the enantiomeric structure.

the Co–N(2) and Co–N(3) bonds, 1.920(5)—1.952(4) Å. The fairly large distortion from the regular octahedron indicates a strained structure of the $N_4$8 ligand involving the planar arrangement of three five-membered chelate rings[8] and a medium-sized eight-membered chelate ring.[1,9]

The conformations of the eight-membered chelate rings in **1** and **2** are similar and take a distorted boat–boat (BB) form, which can be assigned from the endocyclic torsion angles.[6] On the other hand, the conformation is disordered in **3** and **4**. A distorted twist-boat–chair (TBC) form (60%) is also observed besides the BB one (40%) at room temperature, although the central C(9) atom in the TBC form of **3** occupies two possible positions in the ratio of 2:1 (Fig. 2 and Table 2). At 113 K, the population of the TBC form in **4b** is estimated to be 100%, where the central C(9) atom occupies two possible positions in the ratio of 3:2. The temperature dependence of the population in **4a** and **4b** suggests that the BB form is slightly less stable than the TBC form in crystals of the orthorhombic modification. It is reported that the conformational disorder of ethylenediamine (en) chelate rings (δ or λ) in $[Cr(en)_3](SCN)_3 \cdot 0.75H_2O$ at 293 K disappears at 113 K, forming the lel_3 ($\Lambda(\delta\delta\delta)$, $\Delta(\lambda\lambda\lambda)$) conformation.[10] Conformational studies of the five-, six-, and seven-membered chelate rings revealed that the chelate rings become more flexible in this order.[11] The above observations indicate that the eight-membered chelate rings are more flexible and sensitive to the molecular environment. The molecular-mechanics calculation is needed for further discussion on the flexibility of the eight-membered chelate ring.[12]

The electronic spectra in the d–d transition region of green **2** and brown **4** crystals are shown in Fig. 3. The lowest energy band (**2**: 15700 cm^{-1}, **4**: 15400 cm^{-1}) can be assigned to one split component (Ia) of the first d–d band, and the two shoulders around 20000—25000 cm^{-1} (**2**: ca. 21000 and 22500 cm^{-1}, **4**: ca. 20500 and 22000 cm^{-1}) to the other split component (Ib) and the second d–d band, respectively. All the bands of **2** are shifted by 300—700 cm^{-1} towards higher energy than the corresponding bands of **4** at either temperature. The complex in CH_3CN solution shows the corresponding bands at 15800, 20900, and 22700 cm^{-1}.[1] At 113 K, the bands of both **2** and **4** show a small blue shift (ca. 100 cm^{-1}), and become a little sharp with appearance of a new band around 26000 cm^{-1}. The origin of the new band is not clear, but the band may be assigned to a split component of the second d–d band. No apparent spectral difference is seen between green **2** and brown **4**.

Table 2. Positional Parameters ($\times10^4$; $\times10^5$ for Co of **2**) and Equivalent Isotropic Temperature Factors[7]

	X	Y	Z	B/B_{eq}(Å²)×10
		1		
Co	2999(1)	0[a]	2096(1)	23
Cl(1)	3009(1)	1262(1)	4423(1)	33
Cl(2)	2949(1)	−1275(1)	−242(2)	38
O(1)	−2527(5)	−27(6)	−1878(7)	64
O(2)	−3411(5)	−1383(5)	−559(9)	75
O(3)	−1219(5)	−1307(5)	−804(8)	62
N(1)	3348(4)	−1143(4)	4167(6)	33
N(2)	5014(3)	37(5)	2055(5)	35
N(3)	3031(4)	1202(4)	339(5)	31
N(4)	912(3)	93(4)	1656(5)	28
N(5)	−2384(5)	−910(4)	−1067(6)	37
C(1)	4892(6)	−1262(6)	4525(9)	47
C(2)	5648(5)	−258(6)	3969(8)	46
C(3)	5422(5)	1052(6)	1206(8)	41
C(4)	4381(6)	1246(5)	−466(7)	40
C(5)	1753(6)	1164(5)	−983(7)	38
C(6)	578(5)	1019(5)	302(8)	38
C(7)	−74(5)	182(6)	3189(7)	42
C(8)	200(7)	−523(6)	4918(8)	45
C(9)	127(9)	−1724(6)	4724(10)	59
C(10)	1148(7)	−2287(5)	3547(8)	46
C(11)	2678(7)	−2220(5)	4126(9)	47
		2		
Co	30550(4)	0[a]	23358(6)	23
Cl(1)	3107(1)	1093(1)	4849(1)	34
Cl(2)	3015(1)	−1118(1)	−191(1)	37
N(1)	3351(4)	−1198(3)	4196(5)	35
N(2)	5019(3)	23(4)	2294(4)	35
N(3)	3090(3)	1240(2)	739(4)	28
N(4)	1013(3)	126(3)	1945(4)	26
C(1)	4869(5)	−1373(4)	4505(8)	51
C(2)	5646(4)	−381(4)	4113(7)	47
C(3)	5447(4)	1060(4)	1616(7)	41
C(4)	4442(4)	1336(4)	−18(6)	39
C(5)	1851(4)	1267(3)	−561(5)	33
C(6)	705(4)	1067(3)	705(6)	34
C(7)	88(4)	168(4)	3516(6)	40
C(8)	344(5)	−608(4)	5116(7)	45
C(9)	175(6)	−1773(4)	4672(8)	56
C(10)	1162(5)	−2257(4)	3387(7)	46
C(11)	2664(5)	−2247(4)	4008(8)	50
B	7706(5)	−946(4)	9021(8)	40
F(1)	7557(4)	79(3)	8459(5)	74
F(2)	7378(4)	−1617(3)	7569(5)	78
F(3)	9069(3)	−1146(3)	9507(5)	69
F(4)	7030(5)	−1193(4)	10549(8)	103
		3		
Co	4707(1)	3758(1)	3562(1)	34
Cl(1)	3831(2)	4385(1)	4674(2)	48
Cl(2)	5635(2)	3131(1)	2508(2)	53
N(1)	5917(6)	4353(4)	3674(6)	48
N(2)	4358(6)	4199(3)	2260(6)	42
N(3)	3387(6)	3349(4)	3304(6)	40
N(4)	4891(6)	3151(4)	4767(6)	44
C(1)	5864(10)	4746(5)	2662(10)	67
C(2)	4774(10)	4816(4)	2345(9)	58
C(3)	3244(9)	4110(5)	2010(8)	58
C(4)	3043(8)	3452(6)	2195(8)	56
C(5)	3438(9)	2744(5)	3694(9)	57
C(6)	3892(9)	2794(5)	4829(9)	59
C(7)	5229(13)	3310(7)	5892(9)	90
C(8A)[b]	6438(16)	3285(9)	6060(15)	61
C(8B)[c]	5998(27)	3809(16)	6094(20)	77

Table 2. Table 2. (Continued)

	X	Y	Z	B/B_{eq}(Å²)×10
C(9A)[c]	6788(27)	3962(15)	5836(21)	70
C(9B)[d]	7056(61)	3359(29)	5260(58)	92
C(9C)[c]	7061(30)	3597(16)	5436(24)	90
C(10A)[b]	7371(15)	4129(10)	5034(15)	61
C(10B)[c]	7228(23)	3689(14)	4422(23)	68
C(11)	7045(9)	4159(7)	3797(10)	77
B	4463(3)	3685(2)	−798(3)	−14
F(1)	3989(8)	3239(5)	−425(7)	131
F(2)	4848(9)	3985(5)	−88(9)	135
F(3)	3824(9)	3969(5)	−1287(12)	186
F(4)	5068(12)	3553(5)	−1343(9)	174
		4a		
Co	4709(1)	3756(1)	3580(1)	29
Cl(1)	3833(2)	4386(1)	4688(2)	43
Cl(2)	5629(2)	3133(1)	2530(2)	46
Cl(3)	543(2)	3695(1)	4218(2)	45
O(1)	−232(8)	3530(5)	3539(9)	130
O(2)	83(8)	4035(5)	5009(7)	120
O(3)	1067(7)	3191(4)	4653(7)	95
O(4)	1235(7)	4043(5)	3695(11)	160
N(1)	5917(5)	4345(3)	3704(6)	41
N(2)	4350(5)	4194(3)	2278(5)	36
N(3)	3401(6)	3348(3)	3331(5)	38
N(4)	4923(5)	3150(3)	4772(6)	40
C(1)	5879(8)	4754(5)	2723(9)	58
C(2)	4774(9)	4806(4)	2336(8)	57
C(3)	3229(7)	4120(5)	2024(8)	46
C(4)	3068(7)	3464(5)	2190(8)	58
C(5)	3454(7)	2735(4)	3733(8)	48
C(6)	3930(8)	2789(5)	4841(8)	56
C(7)	5217(9)	3286(6)	5899(8)	75
C(8A)[b]	6413(13)	3288(8)	6063(13)	48
C(8B)[c]	5997(27)	3785(17)	6026(18)	90
C(9A)[b]	6886(18)	3939(11)	5694(18)	101
C(9B)[c]	7077(18)	3476(14)	5365(23)	67
C(10A)[b]	7373(13)	4151(8)	5023(14)	53
C(10B)[c]	7210(21)	3628(17)	4479(23)	86
C(11)	7054(7)	4166(6)	3843(9)	72
		4b		
Co	4718(1)	3755(1)	3569(1)	19
Cl(1)	3818(2)	4377(1)	4685(2)	28
Cl(2)	5666(2)	3134(1)	2516(2)	31
Cl(3)	505(2)	3691(1)	4170(2)	24
O(1)	−372(8)	3528(5)	3566(10)	73
O(2)	122(9)	4072(5)	4976(8)	72
O(3)	1017(7)	3176(4)	4612(7)	49
O(4)	1226(8)	3992(5)	3531(12)	96
N(1)	5945(6)	4341(4)	3722(7)	29
N(2)	4382(6)	4197(3)	2257(7)	19
N(3)	3373(7)	3351(4)	3298(6)	19
N(4)	4881(7)	3137(5)	4774(7)	33
C(1)	5901(10)	4744(6)	2722(10)	43
C(2)	4766(10)	4827(5)	2353(10)	36
C(3)	3254(8)	4126(5)	1989(9)	23
C(4)	3045(8)	3457(6)	2155(9)	30
C(5)	3438(9)	2728(5)	3662(10)	33
C(6)	3882(10)	2776(5)	4822(9)	36
C(7)	5237(12)	3271(10)	5917(10)	78
C(8)	6433(11)	3286(7)	6052(11)	54
C(9A)[b]	6576(23)	3957(10)	5986(16)	56
C(9B)[c]	7207(24)	3484(14)	5184(26)	36
C(10)	7351(12)	4115(9)	5124(14)	70
C(11)	7073(11)	4136(7)	3922(12)	50

a) This parameter was used to define the origin of B axis and listed without e.s.d. b—d) Population parameters of disordered carbon atoms: b) 0.6, c) 0.4, d) 0.2.

Table 3. Bond Lengths and Bond Angles

	1	2	3	4a	4b
		Bond length (l/Å)			
Co–Cl(1)	2.257(2)	2.251(1)	2.263(3)	2.268(3)	2.261(3)
Co–Cl(2)	2.272(2)	2.279(1)	2.255(3)	2.245(3)	2.245(3)
Co–N(1)	2.033(4)	2.017(4)	2.048(8)	2.042(8)	2.035(8)
Co–N(2)	1.952(3)	1.939(3)	1.943(7)	1.947(7)	1.943(8)
Co–N(3)	1.930(4)	1.938(3)	1.949(8)	1.933(8)	1.951(9)
Co–N(4)	2.020(3)	2.017(3)	2.031(8)	2.029(7)	2.038(10)
N(1)–C(1)	1.501(7)	1.512(6)	1.532(14)	1.526(14)	1.528(15)
N(1)–C(11)	1.473(8)	1.495(6)	1.517(14)	1.518(11)	1.510(16)
N(2)–C(2)	1.481(7)	1.475(6)	1.483(12)	1.473(11)	1.490(13)
N(2)–C(3)	1.452(9)	1.473(7)	1.474(14)	1.485(11)	1.471(13)
N(3)–C(4)	1.467(7)	1.478(5)	1.461(13)	1.501(12)	1.490(13)
N(3)–C(5)	1.486(6)	1.472(5)	1.438(14)	1.466(11)	1.461(14)
N(4)–C(6)	1.503(7)	1.499(5)	1.511(14)	1.511(13)	1.497(16)
N(4)–C(7)	1.503(6)	1.490(5)	1.502(14)	1.481(14)	1.512(16)
C(1)–C(2)	1.502(10)	1.510(7)	1.460(18)	1.505(15)	1.516(18)
C(3)–C(4)	1.505(7)	1.505(6)	1.511(17)	1.493(16)	1.527(17)
C(5)–C(6)	1.521(8)	1.514(6)	1.526(16)	1.502(14)	1.543(17)
C(7)–C(8)	1.501(9)	1.506(7)			
C(8)–C(9)	1.484(10)	1.518(7)			
C(9)–C(10)	1.509(11)	1.511(8)			
C(10)–C(11)	1.505(10)	1.512(7)			
		Bond angle (ϕ/°)			
Cl(1)–Co–Cl(2)	179.0(1)	179.44(4)	177.52(11)	177.70(11)	177.52(11)
Cl(1)–Co–N(1)	87.8(1)	87.5(1)	86.1(3)	86.0(2)	86.2(2)
Cl(1)–Co–N(2)	92.9(2)	92.3(1)	94.4(2)	94.3(2)	95.1(3)
Cl(1)–Co–N(3)	86.7(1)	87.6(1)	87.7(2)	87.7(2)	87.1(3)
Cl(1)–Co–N(4)	91.0(1)	91.3(1)	91.4(2)	92.3(2)	91.1(3)
Cl(2)–Co–N(1)	92.2(1)	91.9(1)	92.5(2)	92.5(2)	92.5(2)
Cl(2)–Co–N(2)	88.1(2)	87.5(1)	87.5(2)	87.3(2)	86.9(3)
Cl(2)–Co–N(3)	93.6(1)	92.9(1)	94.1(3)	94.0(2)	94.6(3)
Cl(2)–Co–N(4)	88.1(1)	89.1(1)	87.1(3)	86.4(2)	87.3(3)
N(1)–Co–N(2)	85.4(2)	85.7(1)	84.3(3)	85.2(3)	85.3(3)
N(1)–Co–N(3)	168.2(2)	169.6(1)	166.6(3)	167.3(3)	167.1(4)
N(1)–Co–N(4)	104.8(2)	104.0(1)	107.2(3)	105.9(3)	106.8(4)
N(2)–Co–N(3)	84.5(2)	85.2(1)	84.4(3)	84.2(3)	84.3(4)
N(2)–Co–N(4)	169.3(2)	169.7(1)	167.4(3)	167.5(3)	166.8(4)
N(3)–Co–N(4)	85.8(2)	85.3(1)	84.7(3)	85.4(3)	84.4(4)
Co–N(1)–C(1)	107.0(4)	107.3(3)	106.5(6)	107.7(6)	105.9(6)
Co–N(1)–C(11)	124.0(3)	124.9(3)	122.9(7)	124.8(6)	122.8(7)
C(1)–N(1)–C(11)	110.2(5)	108.6(4)	106.8(8)	106.1(7)	109.8(9)
Co–N(2)–C(2)	108.7(3)	109.5(3)	109.3(6)	109.9(5)	109.9(6)
Co–N(2)–C(3)	109.4(4)	109.2(3)	109.2(6)	110.3(5)	110.2(6)
C(2)–N(2)–C(3)	118.7(5)	118.8(4)	119.3(7)	118.0(7)	115.8(7)
Co–N(3)–C(4)	109.8(3)	109.5(2)	110.0(6)	108.3(5)	109.4(6)
Co–N(3)–C(5)	108.8(3)	109.4(2)	110.3(6)	110.0(6)	109.7(7)
C(4)–N(3)–C(5)	118.6(4)	120.0(3)	118.6(8)	119.9(7)	117.2(8)
Co–N(4)–C(6)	107.5(3)	107.4(2)	107.0(6)	106.3(6)	107.9(7)
Co–N(4)–C(7)	125.3(3)	124.2(2)	123.9(7)	125.9(6)	125.4(8)
C(6)–N(4)–C(7)	106.6(4)	107.4(3)	108.8(8)	106.2(7)	108.6(9)
N(1)–C(1)–C(2)	112.0(5)	111.2(4)	108.9(10)	109.3(8)	110.4(10)
N(2)–C(2)–C(1)	105.4(5)	105.4(3)	105.3(8)	106.9(8)	102.5(9)
N(2)–C(3)–C(4)	105.8(4)	105.6(4)	105.3(9)	102.1(8)	104.0(9)
N(3)–C(4)–C(3)	104.5(4)	105.2(3)	104.2(9)	105.1(8)	103.5(9)
N(3)–C(5)–C(6)	104.7(4)	104.4(3)	105.0(9)	104.8(7)	103.9(9)
N(4)–C(6)–C(5)	109.5(4)	110.6(3)	108.4(9)	109.5(8)	107.9(9)
N(4)–C(7)–C(8)	117.5(5)	117.3(4)			
C(7)–C(8)–C(9)	119.7(6)	118.2(4)			
C(8)–C(9)–C(10)	118.6(6)	117.0(5)			
C(9)–C(10)–C(11)	120.0(6)	118.9(4)			
N(1)–C(11)–C(10)	118.4(5)	117.4(4)			

Table 4. Interatomic Hydrogen Bonds

A···H–B (Symmetry code)	*l*/Å		
	A···B	A···H	H–B
1			
O(2)···N(2) (i)	3.037(8)		
O(2)···H(N3)–N(3) (ii)	2.992(8)	2.19(5)	1.02(5)
O(3)···H(N4)–N(4) (iii)	3.103(6)	2.30(5)	0.96(5)
2			
F(2)···H(N3)–N(3) (iv)	3.021(5)	2.41(3)	0.64(3)
F(3)···H(N4)–N(4) (v)	2.958(4)	2.24(4)	0.87(4)
F(4)···H(N2)–N(2) (vi)	2.864(6)	2.10(4)	1.01(5)
3			
F(3)···H(N3)–N(3) (vii)	3.195(14)	2.37(8)	0.97(8)
4a			
O(2)···H(N2)–N(2) (viii)	2.933(11)	2.26(9)	0.84(8)
4b			
O(2)···H(N2)–N(2) (viii)	2.901(13)	2.31(1)	0.89(5)

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

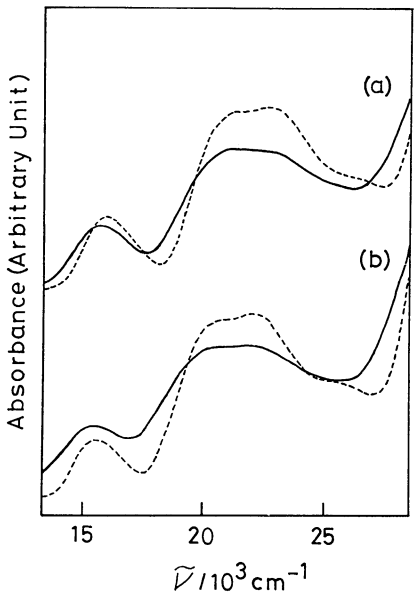

Fig. 3. Electronic spectra in the solid state for (a), *trans*-[$CoCl_2(N_48)$]BF_4 (green) and (b), *trans*-[$CoCl_2(N_48)$]-ClO_4 (brown) at 303 K (——) and 113 K (-----).

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