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Preparation and X-Ray Crystal Structure of *trans*-Dinitro(1,4,7,10-tetraazacycloheptadecane)cobalt(III) Tetrafluoroborate, *trans*-[Co(NO_2)$_2$($N_4$10)]BF_4

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Synopsis. A new tetraaza-macrocyclic complex involving a ten-membered chelate ring, *trans*-[Co(NO_2)$_2$($N_4$10)]BF_4 ($N_4$10=1,4,7,10-tetraazacycloheptadecane) was prepared and the structure was determined by the X-ray diffraction method. The ten-membered chelate ring takes a distorted boat-chair-boat form with the N-Co-N bite angle of 105.4(1)°.

In previous papers,¹⁻³⁾ we reported the preparation and characterization of 1,4,7,10-tetraazacyclotetradecane ($N_4$7), -pentadecane ($N_4$8), and -hexadecane ($N_4$9) complexes of Co(III), which involve a seven-, eight-, and nine-membered chelate ring, respectively. In this note, we report the preparation and crystal structure of a new *trans*-dinitrocobalt(III) complex with 1,4,7,10-tetraazacycloheptadecane ($N_4$10) which involves a ten-membered chelate ring.

Experimental

1,4,7,10-Tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazacycloheptadecane (1) and 1,4,7,10-Tetraazacycloheptadecane Trihydrobromide (2). **1** was prepared by a method similar to those for analogous cyclotetradecane, -pentadecane, and -hexadecane.4) ^{13}C NMR ($CDCl_3$, TMS) δ=21.5($\underline{\text{C}}$-Ts-), 25.3, 27.2, 28.0(C-$\underline{\text{C}}$-C), 48.7, 49.9, 50.2, 50.7(N-$\underline{\text{C}}$-C), 127.3, 127.4, 129.6, 129.8, 135.1, 135.2, 143.3, 143.6(phenyl). **1** was detosylated by refluxing in a mixture of 47% hydrobromic acid and acetic acid for 2 d to give **2**, which was recrystallized from water and ethanol. Found: C, 32.08; H, 6.89; N, 11.41%. Calcd for $C_{13}H_{33}N_4Br_3$: C, 32.19; H, 6.86; N, 11.55%. ^{13}C NMR (D_2O, dioxane(δ=67.4)) δ=24.9, 26.7(C-$\underline{\text{C}}$-C), 44.3, 45.3, 46.8, 47.6(N-$\underline{\text{C}}$-C).

***trans*-[Co(NO_2)$_2$($N_4$10)]BF_4.** This complex was prepared by oxidizing an aqueous solution containing $CoCl_2\cdot 6H_2O$, $NaNO_2$ and $N_4$10 with air according to a method similar to those for the corresponding $N_4$8 and $N_4$9 complexes.1) Found: C, 32.67; H, 6.35; N, 17.72%. Calcd for $C_{13}H_{30}N_6O_4Br_4Co$: C, 32.52; H, 6.30; N, 17.50%. ^{13}C NMR (DMSO-d_6, TMS) δ=22.0, 26.1, 27.2(C-$\underline{\text{C}}$-C), 49.8, 52.4, 54.3, 56.5(N-$\underline{\text{C}}$-C). Electronic spectra {in CH_3CN, $\tilde{\nu}/10^3$ cm^{-1} (log(ε/mol^{-1} dm^3 cm^{-1}))}: 21.5(2.53), 28.2(3.59), 38.7(4.36).

^{13}C NMR spectra were obtained on a Hitachi R-90HS spectrometer, and electronic spectra on a Hitachi U-3400 spectrophotometer.

Crystal Structure Determination. Crystals of *trans*-[Co(NO_2)$_2$($N_4$10)]BF_4 were grown by slow evaporation of an aqueous solution of the complex. An orange crystal of approximate dimensions 0.83×0.43×0.63 mm^3 was used for the measurement.

Crystal Data: *trans*-[Co(NO_2)$_2$($C_{13}H_{30}N_4$)]BF_4, MW=480.2, monoclinic, $P2_1/n$, a=11.982(1), b=19.340(2), c=9.698(1) Å, β=113.63(1)°, V=2059.0(4) Å^3, Z=4, D_c=1.549 g cm^{-3}, D_m=1.55 g cm^{-3}, μ(Mo$K\alpha$)=8.955 cm^{-1}. Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo$K\alpha$ radiation (λ=0.71069 Å). The ω-2θ scan technique was employed with the scan rate 4/°min^{-1} and the scan range 1.2+0.5tanθ/°. Within the range 2θ<60°, 6124 independent reflections were measured. No absorption correction was applied.

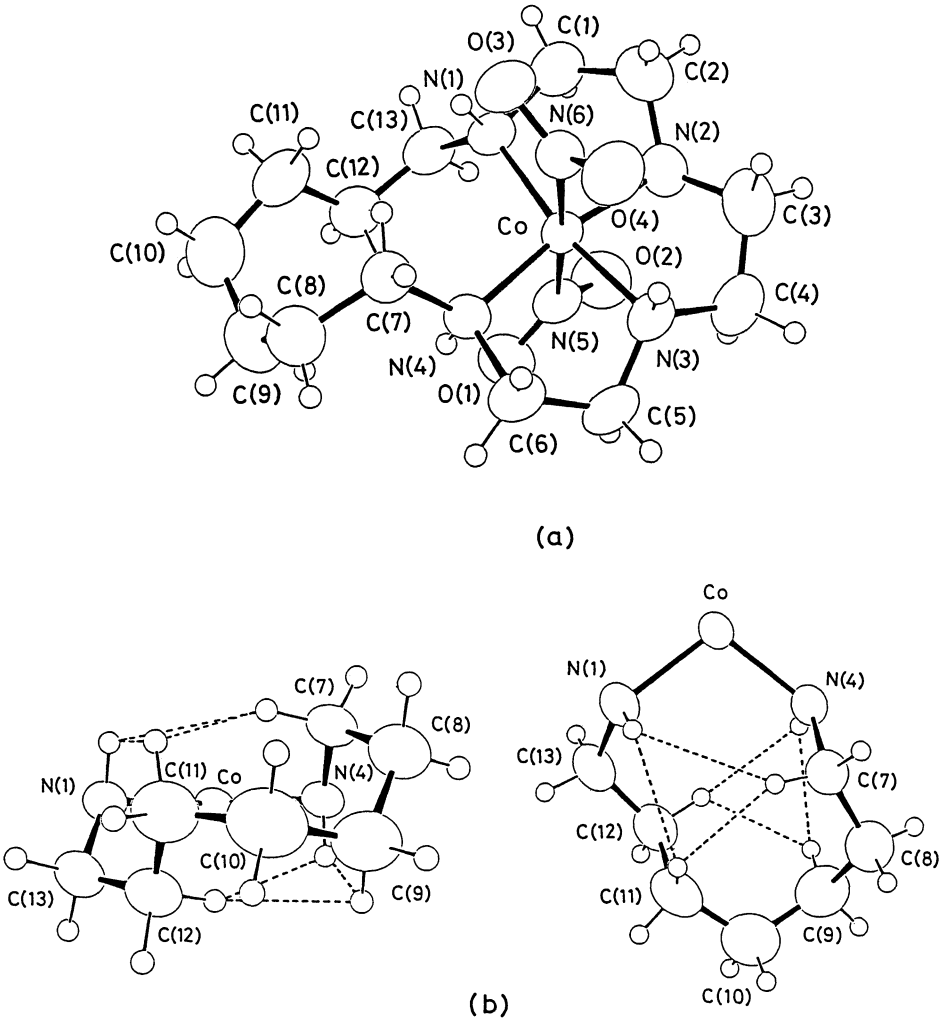
Table 1. Positional Parameters (×10^4; ×10^5 for Co) and Equivalent Isotropic Temperature Factors8)

Atom	x	y	z	B_{eq}/Å^2
Co	26722(3)	15241(2)	42579(4)	2.6
F(1)	8167(5)	1180(2)	3606(4)	9.6
F(2)	8627(14)	1262(4)	6012(7)	26.6
F(3)	7423(5)	2032(3)	4541(7)	12.6
F(4)	9200(6)	2004(6)	5050(9)	18.3
O(1)	1305(2)	1980(2)	1320(3)	5.0
O(2)	266(2)	1929(2)	2627(3)	5.4
O(3)	4260(2)	510(1)	6024(3)	4.7
O(4)	4845(2)	1518(2)	6853(3)	5.5
N(1)	1947(2)	554(1)	3849(3)	3.4
N(2)	1757(2)	1617(2)	5497(3)	3.9
N(3)	3254(2)	2445(1)	4937(3)	3.5
N(4)	3676(2)	1604(1)	3035(3)	3.0
N(5)	1255(2)	1864(1)	2537(3)	3.6
N(6)	4098(2)	1139(1)	5920(3)	3.3
C(1)	1285(4)	444(2)	4865(5)	5.0
C(2)	1712(4)	937(3)	6168(5)	5.1
C(3)	2188(4)	2232(3)	6492(5)	5.4
C(4)	2438(4)	2782(2)	5551(5)	4.9
C(5)	3527(3)	2806(2)	3767(5)	4.3
C(6)	4286(3)	2306(2)	3333(4)	4.1
C(7)	4569(3)	1044(2)	3124(4)	3.6
C(8)	4832(4)	963(2)	1722(5)	4.9
C(9)	3777(4)	722(3)	290(5)	5.6
C(10)	3337(5)	−24(3)	291(6)	6.4
C(11)	2672(4)	−188(2)	1307(5)	5.3
C(12)	1674(3)	318(2)	1157(4)	4.4
C(13)	1143(3)	283(2)	2326(4)	4.3
B	8255(5)	1564(3)	4824(6)	5.5

The calculations were carried out on a HITAC M-680H computer at the Computer Center of Institute for Molecular Science with the program system UNICS III.5) The structure was solved by the heavy-atom method using 4831 unique reflections with $|F_o|>3\sigma(|F_o|)$. The function $\sum w(|F_o|-|F_c|)^2$ was minimized by block-diagonal least-squares with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. Complex neutral-atom scattering factors were used.6) The positions of all hydrogen atoms were identified in the difference synthesis. Final R and R_w were 0.057 and 0.061, respectively. The atomic parameters of non-hydrogen atoms are listed in Table 1.7)

Results and Discussion

The [Co(NO_2)$_2$($N_4$10)]$^+$ complex shows three signals for C-$\underline{\text{C}}$-C and four signals for N-$\underline{\text{C}}$-C groups in the ^{13}C NMR spectrum and can be assigned as the *trans*-isomer with either C_2 or C_s symmetry.1) In the elec-



(a)

(b)

Fig. 1. ORTEP drawings[9] of (a) *trans*-[Co(NO$_2$)$_2$(N$_4$10)]$^+$ and (b) views of the ten-membered chelate ring.

Table 2. Selected Intra- and Intermolecular Distances and Bond Angles

Distance (l/Å)				Bond angles (ϕ/°)			
Co–N(1)	2.040(3)	N(3)–C(4)	1.483(6)	N(1)–Co–N(2)	84.4(1)	C(4)–N(3)–C(5)	119.1(3)
Co–N(2)	1.933(4)	N(3)–C(5)	1.477(6)	N(1)–Co–N(3)	169.5(1)	Co–N(4)–C(6)	108.4(2)
Co–N(3)	1.930(3)	N(4)–C(6)	1.513(5)	N(1)–Co–N(4)	105.4(1)	Co–N(4)–C(7)	119.5(2)
Co–N(4)	2.005(3)	N(4)–C(7)	1.501(5)	N(1)–Co–N(5)	89.3(1)	C(6)–N(4)–C(7)	111.0(3)
Co–N(5)	1.957(2)	C(1)–C(2)	1.500(7)	N(1)–Co–N(6)	88.5(1)	Co–N(5)–O(1)	121.5(2)
Co–N(6)	1.965(2)	C(3)–C(4)	1.508(7)	N(2)–Co–N(3)	85.4(1)	Co–N(5)–O(2)	120.4(3)
O(1)–N(5)	1.227(5)	C(5)–C(6)	1.499(6)	N(2)–Co–N(4)	170.0(1)	O(1)–N(5)–O(2)	118.0(3)
O(2)–N(5)	1.229(4)	C(7)–C(8)	1.522(7)	N(2)–Co–N(5)	89.1(1)	Co–N(6)–O(3)	119.9(2)
O(3)–N(6)	1.231(4)	C(8)–C(9)	1.529(6)	N(2)–Co–N(6)	92.8(1)	Co–N(6)–O(4)	121.1(2)
O(4)–N(6)	1.228(4)	C(9)–C(10)	1.536(8)	N(3)–Co–N(4)	84.8(1)	O(3)–N(6)–O(4)	119.0(3)
N(1)–C(1)	1.507(7)	C(10)–C(11)	1.529(9)	N(3)–Co–N(5)	93.0(1)	N(1)–C(1)–C(2)	111.7(4)
N(1)–C(13)	1.497(4)	C(11)–C(12)	1.506(7)	N(3)–Co–N(6)	89.6(1)	N(2)–C(2)–C(1)	104.8(4)
N(2)–C(2)	1.478(6)	C(12)–C(13)	1.508(7)	N(4)–Co–N(5)	89.5(1)	N(2)–C(3)–C(4)	105.8(4)
N(2)–C(3)	1.486(6)			N(4)–Co–N(6)	89.1(1)	N(3)–C(4)–C(3)	104.8(3)
				N(5)–Co–N(6)	176.9(1)	N(3)–C(5)–C(6)	104.9(3)
O(1)···N(4)	2.753(3)	O(1)···HN(4)	2.10(3)	Co–N(1)–C(1)	107.3(2)	N(4)–C(6)–C(5)	109.4(3)
O(2)···N(2)	2.705(4)	O(2)···HN(2)	2.05(4)	Co–N(1)–C(13)	124.7(2)	N(4)–C(7)–C(8)	114.8(3)
O(3)···N(1)	2.730(3)	O(2)···HN(2)	2.05(3)	C(1)–N(1)–C(13)	107.3(3)	C(7)–C(8)–C(9)	116.8(4)
O(4)···N(3)	2.733(4)	O(4)···HN(3)	2.02(3)	Co–N(2)–C(2)	108.7(3)	C(8)–C(9)–C(10)	116.5(4)
F(4)···N(2)	3.012(8)	F(4)···HN(2)	2.21(5)	Co–N(2)–C(3)	110.0(3)	C(9)–C(10)–C(11)	117.6(5)
HN(1)···HC(7)	2.46(7)	HN(1)···HC(11)	2.34(8)	C(2)–N(2)–C(3)	119.4(3)	C(10)–C(11)–C(12)	113.6(4)
HN(4)···HC(9)	2.22(6)	HN(4)···HC(12)	2.11(5)	Co–N(3)–C(4)	109.6(2)	C(11)–C(12)–C(13)	117.1(4)
HC(7)···HC(11)	2.08(6)	HC(9)···HC(12)	2.15(7)	Co–N(3)–C(5)	109.6(2)	N(1)–C(13)–C(12)	115.3(3)

tronic spectrum, the complex gives two strong charge-transfer bands at 28200 and 38700 cm^{-1}. The positions and intensities of these bands are similar to those for *trans*-$[\mathrm{Co(NO_2)_2(N_4}x)]^+$($x$=7, 8, 9).[1] The *cis*-$[\mathrm{Co(NO_2)_2(N_4}x)]^+$($x$=5, 6, 7) isomers show both of them at higher energy, ca. 30000 and 40000 cm^{-1}.[1] The *trans*-isomer of the present complex was confirmed by the X-ray structure determination described below.

A perspective view of the complex cation is shown in Fig. 1(a). Table 2 lists the selected bond distances and angles together with the short interatomic distances. The complex is a *trans*-dinitro isomer. The four chiral amino nitrogen atoms have an RSSR(SRRS) configuration. The same chiralities of the four nitrogen atoms have been found for analogous N$_4x$ complexes, *trans*-$[\mathrm{NiCl_2(N_47)}]$,[10] $[\mathrm{Cu(N_47)}]^{2+}$,[11] *trans*-$[\mathrm{CoCl_2(N_48)}]^+$,[2] and *trans*-$[\mathrm{NiCl_2(N_49)}]$.[10] The two $\mathrm{NO_2^-}$ ions coordinate to the Co(III) through the nitrogen atom and are oriented toward the nitrogen atoms of the macrocycle to form short O ··· HN hydrogen bondings (2.02—2.10 Å). The Co–NO$_2$ bond lengths (1.957(2) and 1.965(2) Å) are a little longer than those found in *trans*-dinitro Co(III) complexes, such as *trans*-$[\mathrm{Co(NO_2)_2(NH_2CH_2CH_2NH_2)_2}]^+$ (av. 1.938(2) Å)[12] and *trans*-$[\mathrm{Co(NO_2)_2(NH_2CH_2CH_2CH_2CH_2NH_2)_2}]^+$ (av. 1.934(4) Å).[13] The lengthening of the Co–NO$_2$ bonds may be attributed to the steric repulsion between the $\mathrm{NO_2^-}$ ion and the methylene protons as observed short O ··· HC distances (2.45(4)—2.70(4) Å). The bond distances of Co–N(1)(2.040(3) Å) and Co–N(4)(2.005(3) Å) for the ten-membered chelate ring are longer by ca. 0.09 Å than those of Co–N(2)(1.933(4) Å) and Co–N(3) (1.930(3) Å). The N(1)–Co–N(4) bite angle of the ten-membered chelate ring is 105.4(1)°, while those of three five-membered chelate rings are 84.4(1), 85.4(1), and 84.8(1)°. The same elongation of the Co–N bond and widening of the N–Co–N bite angle have been observed for the eight-membered chelate ring in *trans*-$[\mathrm{CoCl_2(N_48)}]^+$.[2] The fairly large distortion from the regular octahedron is attributable to the strain arising from the planar arrangement of three five-membered chelate rings and the repulsion among hydrogen atoms of the medium-sized ten-membered chelate ring. 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, and that involving a N(2)–C(3)–C(4)–N(3) moiety forms a gauche conformation. The conformation of the ten-membered chelate ring is assigned as a distorted boat-chair–boat (BCB) form as shown in Fig. 1(b). A similar BCB form has been found in 1,6-*cis*-diaminocyclodecane-dihydrochloride.[14] All the bond angles around the nitrogen and carbon atoms of the ten-membered chelate ring are larger than the tetrahedral angle, in particular the Co–N–C angles are large, 124.7(2)° and 119.5(2)°. Trans-annular hydrogen-hydrogen interactions are also observed among the sets of HN(1), HC(7) and HC(11), and of HN(4), HC(9) and HC(12), which are depicted as dashed lines in Fig. 1(b).

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