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Contribution from The Institue for Solid State Physics,
The University of Tokyo, Roppongi-7, Minato-Ku, Tokyo 106, Japan

Atropisomerism in Metal Chelates. Crystal Structure of [(–)$_{589}$-3-(6-Methyl-2,4-dinitrophenyl)pentane-2,4-dionato][tris(2-aminoethyl)amine]cobalt(III) Dibromide Dihydrate[1]

YOSHIHARU NAKANO*[2] and SHOICHI SATO

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The preparation and X-ray structure determination of [(–)$_{589}$-3-(6-methyl-2,4-dinitrophenyl)pentane-2,4-dionato][tris(2-aminoethyl)amine]cobalt(III) dibromide dihydrate are described. The orange-red platey crystals are monoclinic with space group $P2_1$, a = 13.743 (1) Å, b = 7.662 (1) Å, c = 12.623 (1) Å, β = 95.36 (1)°, and Z = 2. The structure was solved by the heavy-atom method and refined by block-diagonal least squares to a final R value of 0.038 for 2926 observed reflections with $|F_0| > 3\sigma(|F_0|)$. The six-membered acac ring adopts a flattened boat form to which the aromatic ring is almost perpendicular. All three five-membered chelate rings formed by tren take on an envelope conformation. One of the chelate rings exhibits a conformational disorder. The ortho nitro group is also orientationally disordered. The absolute configuration of the complex cation can be designated as R.

Introduction

Recently Y.N. has reported syntheses and resolutions of a series of optically active metal chelates whose optical activity arises from restricted rotation of an aromatic ring[3a] as shown in Figure 1. Although the aromatic ring which produces the optical activity lies at a nonligating position apart from the cobalt(III) ion, the rotatory strengths of complexes I and II in their first absorption region are comparable to those of complexes that have dissymmetric arrangements of chelation.[4] The circular dichroism spectrum of [(–)$_{589}$-3-(6-methyl-2,4-dinitrophenyl)pentane-2,4-dionato][tris(2-aminoethyl)amine]cobalt(III) dibromide dihydrate (complex II) shows two peaks in the first absorption region ($\Delta\epsilon$ = –1.22 at 18.6 × 10^3 cm^{-1} and $\Delta\epsilon$ = +1.33 at 20.9 × 10^3 cm^{-1}).[3b]

The rotatory strength depends on the nature of the substituents of the aromatic ring. A molecular model indicates that two further structural effects contribute to the optical rotation: the first is the orientation of the aromatic with respect to the acac ring, and the second is the conformation of the tren chain which contains three dissymmetric chelate rings.

This paper describes the crystal structure and absolute configuration of the title compound.

Experimental Section

Measurements. The infrared and ^{1}H NMR spectra were recorded on Hitachi Model EPI-S2 and R-20 spectrometers, respectively. Optical rotation of the resolved complex was measured with a JASCO DIP-180 automatic polarimeter.

Preparation of the β-Diketone. 1-Chloro-6-methyl-2,4-dinitrobenzene[5] was treated with KF under the same conditions as the preparation of 1-fluoro-2,4-dinitrobenzene from 1-chloro-2,4-dinitrobenzene.[6] The fraction with bp <100 °C (20 mmHg) was discarded. The distillate with a boiling point higher than that point to 155 °C (1.1 mmHg) was assumed to consist mainly of 1-fluoro-6-methyl-2,4-dinitrobenzene and was used for the next coupling reaction without further purification. A mixture of sodium acetylacetonate (12.4 g)[7] and the fluorobenzene (24 g) in 300 mL of acetone (dried with anhydrous $CaSO_4$) was refluxed for 26 h. After acetone was evaporated, the residue was dissolved in benzene, washed twice with water, and dried with Na_2SO_4. From the benzene solution was obtained 5.2 g of β-diketone (18%). It was recrystallized from ethanol; mp 142–143 °C. A small amount of the β-diketone was chromatographed (silica gel) and recrystallized from benzene; mp 144.5–145.5 °C. IR (KBr): broad peak at 1600 cm^{-1} (characteristic of β-diketone); 1540, 1520, and 1345 cm^{-1} (ν_{NO_2}). ^{1}H NMR: τ –6.59 (s, 1 H, enolic hydroxyl proton), 1.46–1.64 (AB quartet, 2 H, aromatic protons), 7.55 (s, 3 H, methyl protons attached to the aromatic ring), 8.17 (s, 6 H, two methyl groups of the acac moiety). Anal. Calcd for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32; N, 9.99. Found: C, 51.40; H, 4.31; N, 9.80.

Preparation of [3-(6-Methyl-2,4-dinitrophenyl)pentane-2,4-dionato][tris(2-aminoethyl)amine]cobalt(III) Ion. This was prepared in the same manner as that of complex I;[3a] yield 57% (estimated from the absorbance in the visible region). IR (KBr); 1565 cm^{-1} (γ-substituted acac ring); 1533 and 1530 cm^{-1} (ν_{NO_2}). ^{1}H NMR (in 0.1 N D_2SO_4 with sodium 3-(trimethylsilyl)-propanesulfonate as an internal standard): τ 1.23 and 1.38 (AB quartet, 2 H, aromatic protons), 4.4–5.4 (amino protons of tren), 6.0–7.3 (methylene protons of tren), 8.00 and 8.02 (s, 6 H, methyl protons of the acac ring). Anal. Calcd for $C_{18}H_{29}N_6O_6Br_2Co\cdot 1.5H_2O$: C, 32.21; H, 4.81; N, 12.52. Found: C, 32.28; H, 5.11; N, 12.57.

Resolution. The complex was resolved by SP Sephadex column chromatography with a 0.5 M sodium (+)$_{589}$-antimonyl tartrate solution as eluant, but the tail of the faster eluting (–)$_{589}$ isomer overlapped with the (+)$_{589}$ band. The fractions of (–)$_{589}$ isomer were collected, diluted 10 times with water, and reloaded on an SP Sephadex column. The adsorbed band was eluted with a 0.5 M NaBr solution. A small amount of the resolved complex was reloaded on an SP Sephadex column to confirm the optical purity. When the solution of resolved bromide complex was condensed slowly at 8 °C, single crystals were obtained easily.

Crystal Examination. The crystals were in the form of orange-red plates. Weissenberg photographs indicated a monoclinic unit cell with systematic extinction for $0k0$, $k = 2n + 1$. Of two possible space groups $P2_1$ and $P2_1/m$, the latter was eliminated because of the optical activity of the compound. The cell dimensions were determined by a least-squares calculation based on 20 θ values measured on a Philips four-circle diffractometer. The cell dimensions are a = 13.743 (1) Å, b = 7.662 (1) Å, c = 12.623 (1) Å, and β = 95.36 (1)°. Comparison of the calculated density (1.75 g/cm^3) with the value of 1.70 g/cm^3 measured by flotation in a mixture of CCl_4 and $C_2H_2Br_4$ proved two molecules per unit cell.

Intensity Data Collection. A crystal was shaped into a sphere 0.48 mm in diameter and used for the intensity measurement. The intensities were collected up to 2θ = 60° by the θ–2θ scan technique at a scan rate of 2° min^{-1} (in θ) with Mo Kα radiation (λ = 0.7107

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(1) The following abbreviations are used: tren, tris(2-aminoethyl)amine; glyH, glycine; acacH, acetylacetone.

(2) To whom correspondence should be addressed at the Faculty of Science, Ibaraki University, Bunkyo, Mito 310, Japan.

(3) (a) Preparation and resolution of complex I had been reported by: Nakano, Y.; Seki, H. *Chem. Lett.* **1976**, 611. (b) Detailed data will be published elsewhere.

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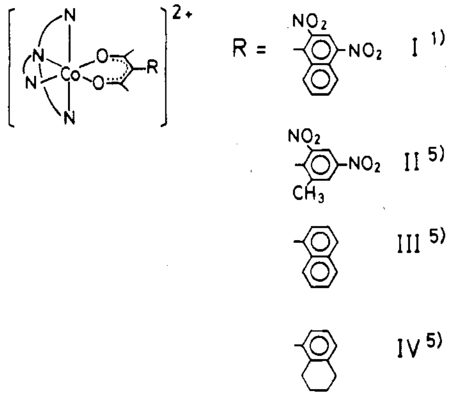

Figure 1. Four complexes of this series.

Å), the scan range being (1.3 ± 0.3 tan θ)°. The background counts were taken before and after each scan. Lorentz–polarization and absorption corrections were applied. In total 3232 independent reflections were measured, of which 2926 with $|F_o| > 3\sigma(|F_o|)$ were used for structure determination.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method: locations of Co and Br atoms were deduced from three-dimensional Patterson maps. Least-squares refinement of these positions resulted in an R value of 0.299. The y coordinate of the Co atom was fixed at 0.5. Positions of all other nonhydrogen atoms were derived by the Fourier method. They were refined by a block-diagonal least-squares program with anisotropic thermal parameters. Finally all the hydrogen atoms were located from difference Fourier maps except two of water molecules; they were also included in the refinement with isotropic thermal parameters. At a later stage of the refinement, a carbon atom of the tren chain and the three atoms of the ortho nitro group showed unusually large thermal parameters; furthermore, extra peaks were found around these atoms on difference Fourier maps. The facts strongly suggested disordered dispositions of the atoms. The disordered model was refined by the full-matrix least squares to final R_1 of 0.038 and R_2 of 0.036, while the ordered structure refined to R_1 = 0.042 and R_2 = 0.040 ($R_1 = \sum|\Delta F|/\sum|F_o|$, $R_2 = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$). Throughout the refinement, unit weight was assigned for all the reflections. The ordered model can be rejected at the 0.005 significance level by Hamilton's R test.[8] The final parameters shifts of the nonhydrogen atoms except those of the nitro group were all less than 0.8σ. The final difference Fourier maps showed no peak greater than 0.5 e Å^{-3}. The positional and thermal parameters along with their standard deviations are listed in Tables I and II, respectively. A compilation of the observed and calculated structure factors is available.[9a] The atomic scattering factors and anomalous scattering corrections were taken from ref 10. The calculations were performed on a FACOM 230-48 computer at this institute with a local version of UNICS (Crystallographic Society of Japan).[11] Some of the calculations were carried out on a HITAC 8800/8700 at the Computer Center of The University of Tokyo.

Determination of the Absolute Configuration. The absolute configuration was determined by anomalous scattering techniques. Some Bijvoet pairs were examined on equiinclination Weissenberg photographs taken with Cu Kα radiation. The observed and calculated differences are compared in Table III, for which $|F(hkl)|$ and $|F(h\bar{k}l)|$ differed by more than 35%.[9b] The concordance in the table indicated that the absolute configuration of the $(-)_{589}$ isomer is R according to Cahn–Ingold–Prelog notation.[12] As a confirmation the enantiomeric structure was refined under the identical conditions without taking account of the disorder; R_1 became 0.047 and R_2 = 0.045.

Table I. Positional Parameters with Their Standard Deviations in Parentheses

atom	x	y	z
Co	0.18972 (5)	0.50000 (13)	0.26621 (6)
Br(1)	0.18541 (6)	0.09501 (16)	0.01694 (6)
Br(2)	0.16629 (5)	0.08298 (13)	0.49798 (6)
C(1)	−0.0162 (4)	0.4493 (10)	0.2430 (5)
C(21) (G_1[a])	0.0269 (6)	0.2820 (16)	0.2095 (9)
C(22) (G_2)	0.0247 (15)	0.2775 (42)	0.2831 (21)
C(3)	0.0510 (4)	0.7116 (9)	0.1613 (5)
C(4)	0.0925 (4)	0.6168 (12)	0.0708 (5)
C(5)	0.0499 (4)	0.6924 (10)	0.3562 (5)
C(6)	0.0897 (4)	0.5818 (12)	0.4475 (4)
C(7)	0.3475 (5)	0.9640 (8)	0.2797 (6)
C(8)	0.3304 (4)	0.7727 (8)	0.2751 (5)
C(9)	0.4067 (3)	0.6548 (8)	0.2626 (4)
C(10)	0.3944 (4)	0.4743 (8)	0.2662 (4)
C(11)	0.4815 (4)	0.3550 (9)	0.2635 (7)
C(12)	0.5059 (4)	0.7291 (8)	0.2486 (4)
C(13)	0.5350 (5)	0.7708 (11)	0.1478 (5)
C(14)	0.6246 (5)	0.8432 (11)	0.1318 (5)
C(15)	0.6860 (4)	0.8752 (10)	0.2207 (5)
C(16)	0.6632 (4)	0.8349 (10)	0.3210 (5)
C(17)	0.5725 (4)	0.7640 (9)	0.3358 (5)
C(18)	0.5496 (5)	0.7226 (14)	0.4464 (5)
N(1)	0.0574 (3)	0.5947 (9)	0.2552 (3)
N(2)	0.1312 (3)	0.2709 (7)	0.2511 (4)
N(3)	0.1842 (3)	0.5314 (7)	0.1120 (4)
N(4)	0.1847 (3)	0.5107 (8)	0.4203 (4)
N(51) (G_3)	0.4721 (8)	0.7105 (17)	0.0534 (8)
N(52) (G_4)	0.4624 (11)	0.7763 (23)	0.0493 (10)
N(6)	0.7827 (4)	0.9504 (9)	0.2070 (5)
O(1)	0.2409 (3)	0.7296 (6)	0.2811 (3)
O(2)	0.3140 (3)	0.3956 (6)	0.2753 (3)
O(31) (G_3)	0.3907 (6)	0.7178 (22)	0.0458 (8)
O(32) (G_4)	0.4032 (15)	0.6543 (33)	0.0484 (12)
O(41) (G_3)	0.5170 (10)	0.6668 (28)	−0.0266 (9)
O(42) (G_4)	0.4601 (13)	0.8797 (35)	−0.0114 (12)
O(5)	0.7976 (4)	1.0079 (10)	0.1205 (4)
O(6)	0.8423 (4)	0.9555 (11)	0.2837 (5)
O(7)	0.3122 (5)	0.7508 (10)	0.5582 (6)
O(8)	0.7200 (6)	0.3690 (16)	0.2089 (10)
H(C1A)	−0.071 (4)	0.493 (10)	0.200 (5)
H(C1B)	−0.026 (6)	0.421 (12)	0.309 (6)
H(C21A)	0.029 (6)	0.302 (14)	0.126 (7)
H(C21B)	−0.012 (4)	0.175 (9)	0.223 (5)
H(N2A)	0.161 (5)	0.206 (10)	0.197 (5)
H(N2B)	0.143 (5)	0.217 (11)	0.308 (6)
H(C3A)	0.091 (4)	0.804 (10)	0.189 (5)
H(C3B)	−0.013 (4)	0.736 (8)	0.135 (4)
H(C4A)	0.094 (5)	0.687 (10)	0.022 (5)
H(C4B)	0.052 (3)	0.548 (7)	0.044 (4)
H(N3A)	0.232 (3)	0.606 (8)	0.095 (4)
H(N3B)	0.199 (5)	0.429 (9)	0.085 (5)
H(C5A)	0.078 (4)	0.783 (9)	0.368 (5)
H(C5B)	−0.008 (5)	0.732 (10)	0.366 (5)
H(C6A)	0.111 (4)	0.634 (9)	0.501 (4)
H(C6B)	0.061 (4)	0.486 (10)	0.470 (5)
H(N4A)	0.232 (4)	0.575 (10)	0.452 (4)
H(N4B)	0.198 (6)	0.363 (12)	0.462 (6)
H(C7)	0.416 (5)	1.005 (12)	0.312 (6)
H(C7)	0.325 (5)	1.023 (11)	0.319 (5)
H(C7)	0.326 (6)	1.028 (13)	0.219 (6)
H(C11)	0.512 (7)	0.412 (14)	0.217 (8)
H(C11)	0.523 (7)	0.389 (15)	0.316 (7)
H(C11)	0.463 (6)	0.256 (13)	0.231 (7)
H(C14)	0.625 (4)	0.882 (9)	0.074 (5)
H(C16)	0.708 (4)	0.850 (7)	0.377 (4)
H(C18)	0.543 (4)	0.592 (11)	0.453 (4)
H(C18)	0.586 (4)	0.799 (8)	0.505 (4)
H(C18)	0.479 (6)	0.742 (14)	0.459 (7)
H(O7)	0.277 (5)	0.727 (11)	0.613 (5)
H(O8)	0.712 (6)	0.412 (13)	0.148 (7)

[a] Population parameters of the disordered atoms: G_1 = 0.80 (3), G_2 = 0.20 (3), G_3 = 0.502 (30), G_4 = 0.498 (30).

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(9) Supplementary material: (a) table of $|F_o|$ and $|F_c|$; (b) observation of some Bijvoet pairs; (c) table of interatomic distances outside the complex ion.

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(12) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

Table II. Thermal Parameters with Their Standard Deviations in Parentheses[a,b]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.0217 (3)	0.0327 (3)	0.0348 (3)	−0.0041 (3)	0.0020 (2)	−0.0007 (4)
Br(1)	0.0639 (4)	0.0694 (5)	0.0550 (4)	−0.0023 (5)	0.0022 (3)	−0.0083 (5)
Br(2)	0.0569 (4)	0.0466 (3)	0.0577 (4)	−0.0025 (4)	0.0168 (3)	−0.0005 (4)
C(1)	0.026 (3)	0.057 (4)	0.052 (4)	−0.008 (3)	0.001 (2)	−0.005 (3)
C(21)	0.032 (4)	0.072 (7)	0.097 (8)	−0.027 (5)	−0.003 (4)	−0.010 (6)
C(22)	0.007 (8)	0.051 (17)	0.033 (13)	−0.006 (10)	0.006 (8)	−0.008 (13)
C(3)	0.035 (3)	0.044 (4)	0.047 (3)	0.002 (3)	−0.006 (3)	0.006 (3)
C(4)	0.043 (3)	0.071 (5)	0.037 (3)	−0.003 (4)	−0.005 (2)	0.008 (4)
C(5)	0.031 (3)	0.052 (4)	0.047 (3)	0.003 (3)	0.007 (2)	−0.011 (3)
C(6)	0.044 (3)	0.063 (4)	0.034 (3)	−0.001 (4)	0.009 (2)	−0.005 (4)
C(7)	0.044 (3)	0.032 (4)	0.078 (5)	−0.009 (3)	0.007 (3)	−0.004 (3)
C(8)	0.029 (3)	0.035 (3)	0.037 (3)	−0.001 (2)	0.004 (2)	−0.001 (3)
C(9)	0.020 (2)	0.035 (3)	0.041 (3)	−0.005 (2)	0.005 (2)	−0.002 (3)
C(10)	0.029 (2)	0.030 (3)	0.035 (3)	−0.002 (2)	0.005 (2)	0.001 (2)
C(11)	0.034 (3)	0.029 (3)	0.088 (5)	−0.001 (3)	0.018 (3)	−0.003 (4)
C(12)	0.027 (2)	0.032 (3)	0.038 (3)	−0.007 (2)	0.004 (2)	−0.002 (3)
C(13)	0.042 (3)	0.065 (5)	0.031 (3)	−0.016 (3)	−0.004 (3)	0.003 (3)
C(14)	0.045 (3)	0.071 (5)	0.037 (3)	−0.018 (4)	0.007 (3)	0.012 (3)
C(15)	0.024 (2)	0.051 (4)	0.054 (4)	−0.010 (3)	0.008 (2)	0.005 (3)
C(16)	0.028 (3)	0.057 (4)	0.038 (3)	−0.011 (3)	−0.002 (2)	0.003 (3)
C(17)	0.029 (3)	0.042 (3)	0.038 (3)	−0.007 (3)	0.006 (2)	0.004 (3)
C(18)	0.048 (4)	0.107 (7)	0.034 (3)	−0.028 (5)	0.004 (3)	0.008 (4)
N(1)	0.022 (2)	0.048 (3)	0.039 (2)	−0.002 (3)	0.002 (2)	0.006 (5)
N(2)	0.032 (2)	0.043 (3)	0.040 (3)	−0.009 (2)	0.004 (2)	−0.003 (2)
N(3)	0.036 (2)	0.041 (3)	0.038 (3)	−0.002 (2)	0.006 (2)	0.001 (2)
N(4)	0.033 (2)	0.046 (3)	0.037 (2)	−0.003 (3)	0.001 (2)	0.005 (3)
N(51)	0.067 (7)	0.057 (8)	0.029 (5)	−0.045 (6)	−0.004 (5)	0.011 (5)
N(52)	0.101 (11)	0.097 (13)	0.038 (7)	−0.044 (10)	−0.003 (7)	0.027 (8)
N(6)	0.033 (3)	0.063 (4)	0.073 (4)	−0.020 (3)	0.011 (3)	0.001 (3)
O(1)	0.023 (2)	0.032 (2)	0.053 (2)	−0.002 (2)	0.004 (2)	−0.002 (2)
O(2)	0.024 (2)	0.032 (2)	0.055 (2)	−0.005 (2)	0.001 (2)	0.002 (2)
O(31)	0.031 (4)	0.156 (14)	0.049 (6)	−0.017 (7)	−0.008 (4)	0.011 (8)
O(32)	0.215 (19)	0.270 (29)	0.073 (10)	−0.174 (21)	−0.017 (11)	0.019 (14)
O(41)	0.090 (9)	0.218 (23)	0.058 (8)	−0.033 (12)	0.006 (6)	−0.059 (11)
O(42)	0.161 (18)	0.272 (29)	0.070 (9)	−0.108 (19)	−0.050 (10)	0.085 (14)
O(5)	0.070 (3)	0.119 (5)	0.057 (3)	−0.050 (4)	0.027 (3)	0.001 (4)
O(6)	0.042 (3)	0.153 (8)	0.104 (5)	−0.041 (4)	−0.018 (3)	0.061 (5)
O(7)	0.074 (4)	0.075 (5)	0.125 (6)	−0.005 (4)	−0.026 (4)	0.006 (5)
O(8)	0.105 (7)	0.162 (10)	0.249 (12)	0.000 (7)	0.074 (7)	0.045 (10)

atom	B, Å^2	atom	B, Å^2	atom	B, Å^2	atom	B, Å^2
H(C1A)	4.1 (1.5)	H(C4A)	5.0 (1.8)	H(N4A)	3.5 (1.3)	H(C14)	3.0 (1.3)
H(C1B)	6.5 (2.2)	H(C4B)	1.7 (1.1)	H(N4B)	6.8 (2.2)	H(C16)	1.7 (1.1)
H(C21A)	8.3 (2.5)	H(N3A)	1.7 (1.0)	H(C7)	6.2 (1.9)	H(C18)	3.5 (1.3)
H(C21B)	3.9 (1.5)	H(N3B)	3.9 (1.5)	H(C7)	4.8 (1.7)	H(C18)	2.3 (1.2)
H(N2A)	4.7 (1.7)	H(C5A)	3.3 (1.4)	H(C7)	7.2 (2.3)	H(C18)	8.7 (2.7)
H(N2B)	5.6 (1.9)	H(C5B)	4.3 (1.6)	H(C11)	9.9 (3.0)	H(O7)	5.1 (1.8)
H(C3A)	4.0 (1.6)	H(C6A)	3.2 (1.3)	H(C11)	10.1 (2.9)	H(O8)	8.1 (2.5)
H(C3B)	2.8 (1.3)	H(C6B)	3.9 (1.5)	H(C11)	8.6 (2.7)		

[a] Anisotropic thermal parameters are defined by $\exp[-2\pi^2(h^2U_{11}a^2 + \ldots + 2hkU_{12}ab + \ldots)]$. [b] The isotropic thermal parameter is defined by $\exp[-B\{(\sin\theta)/\lambda\}^2]$.

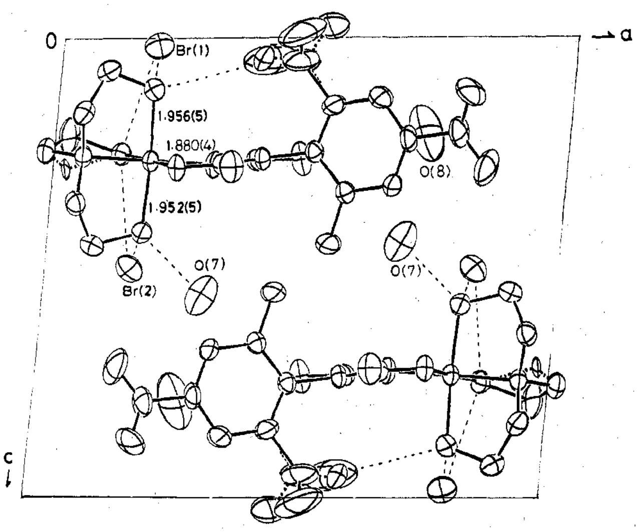

Figure 2. Packing in the unit cell. View is down *b*.

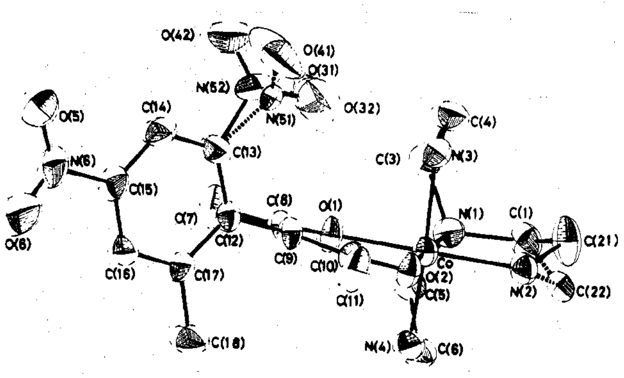

Figure 3. A perspective view of the complex cation.

Application of the *R* factor ratio test shows that this structure can be rejected at the 0.005 level in favor of the *R* configuration.

Description of the Structure and Discussion

Figure 2 shows a projection of the crystal structure along the *b* axis. The crystal consists of complex cations, bromide

Table IV. Bond Lengths (Å) and Angles (Deg) with Their Standard Deviations in Parentheses

	Distances		
Co–N(1)	1.950 (4)	C(10)–O(2)	1.273 (7)
Co–N(2)	1.933 (6)	C(8)–C(9)	1.404 (8)
Co–N(3)	1.956 (5)	C(9)–C(10)	1.394 (8)
Co–N(4)	1.952 (5)	C(10)–C(11)	1.509 (8)
Co–O(1)	1.897 (4)	C(9)–C(12)	1.503 (7)
Co–O(2)	1.880 (4)	C(12)–C(13)	1.406 (8)
C(1)–N(1)	1.503 (9)	C(13)–C(14)	1.382 (10)
C(1)–C(21)	1.490 (14)	C(14)–C(15)	1.362 (9)
C(1)–C(22)	1.500 (31)	C(15)–C(16)	1.368 (9)
C(21)–N(2)	1.483 (9)	C(16)–C(17)	1.388 (8)
C(22)–N(2)	1.555 (22)	C(17)–C(18)	1.493 (9)
C(3)–N(1)	1.482 (9)	C(13)–N(51)	1.479 (12)
C(3)–C(4)	1.510 (10)	C(13)–N(52)	1.520 (14)
C(4)–N(3)	1.471 (8)	C(15)–N(6)	1.473 (8)
C(5)–N(1)	1.491 (8)	N(51)–O(31)	1.116 (14)
C(5)–C(6)	1.492 (10)	N(52)–O(32)	1.239 (29)
C(6)–N(4)	1.511 (8)	N(51)–O(41)	1.276 (17)
C(7)–C(8)	1.485 (9)	N(52)–O(42)	1.101 (27)
C(8)–O(1)	1.282 (7)	N(6)–O(6)	1.208 (8)
N(6)–O(5)	1.212 (9)		
	Angles		
N(1)–Co–N(2)	87.4 (3)	O(1)–C(8)–C(7)	113.7 (6)
N(1)–Co–N(3)	86.2 (3)	O(1)–C(8)–C(9)	124.9 (6)
N(1)–Co–N(4)	87.1 (3)	Co–O(2)–C(10)	125.7 (4)
N(2)–Co–N(3)	92.1 (2)	O(2)–C(10)–C(11)	114.3 (6)
N(2)–Co–N(4)	92.9 (3)	O(2)–C(10)–C(9)	125.6 (6)
N(3)–Co–N(4)	171.4 (3)	C(9)–C(12)–C(13)	122.1 (6)
N(3)–Co–O(1)	88.0 (2)	C(9)–C(12)–C(17)	121.1 (6)
N(3)–Co–O(2)	93.7 (2)	C(8)–C(9)–C(10)	122.7 (6)
N(4)–Co–O(1)	86.7 (2)	C(8)–C(9)–C(12)	117.7 (5)
N(4)–Co–O(2)	93.4 (2)	C(12)–C(13)–C(14)	123.8 (7)
O(1)–Co–O(2)	93.5 (2)	C(12)–C(13)–N(51)	117.6 (8)
Co–N(1)–C(1)	110.2 (5)	C(12)–C(13)–N(52)	121.7 (9)
Co–N(1)–C(3)	105.5 (5)	C(13)–C(14)–C(15)	116.4 (8)
N(1)–C(1)–C(21)	112.7 (7)	C(14)–C(15)–C(16)	122.9 (7)
N(1)–C(1)–C(22)	112.9 (13)	C(16)–C(17)–C(18)	118.7 (7)
C(1)–C(21)–N(2)	110.2 (8)	C(15)–C(16)–C(17)	120.0 (7)
C(1)–C(22)–N(2)	105.8 (20)	C(14)–C(15)–N(6)	118.1 (7)
Co–N(2)–C(21)	111.2 (6)	C(13)–N(51)–O(31)	124.1 (14)
Co–N(2)–C(22)	109.7 (12)	C(13)–N(52)–O(32)	111.6 (17)
Co–N(1)–C(5)	105.4 (5)	O(31)–N(51)–O(41)	120.0 (17)
N(1)–C(3)–C(4)	108.4 (6)	O(32)–N(52)–O(42)	124.0 (24)
C(5)–C(6)–N(4)	108.5 (7)	C(15)–N(6)–O(5)	118.0 (7)
C(3)–C(4)–N(3)	108.6 (7)	O(5)–N(6)–O(6)	123.4 (8)
Co–N(3)–C(4)	111.4 (5)	C(13)–N(51)–O(41)	115.5 (24)
Co–N(4)–C(6)	109.9 (5)	C(13)–N(52)–O(42)	124.3 (20)
N(1)–C(5)–C(6)	109.0 (7)	Co–O(1)–C(8)	125.6 (4)

Table VI. Possible Intracomplex A–H- -B Interactions

			interatomic dist, Å		angle A–H- -B,
A	H	B	A- - -B	B- -H	deg
N(2)	H(5)	Br(1)	3.394 (5)	2.48 (7)	158 (6)
N(3)	H(12)	Br(1)	3.553 (6)	2.70 (7)	162 (6)
N(2)	H(6)	Br(2)	3.425 (5)	2.61 (7)	172 (7)
N(4)	H(17)	O(7)	3.029 (9)	2.13 (6)	164 (6)
N(4)	H(18)	Br(2)	3.372 (6)	2.24 (9)	157 (6)
N(3)	H(11)	O(31)	3.351 (12)	2.48 (5)	161 (4)
N(3)	H(11)	O(32)	3.322 (21)	2.51 (5)	149 (4)

ions, and water molecules. The complex cations seem to be loosely packed around the aromatic ring as reflected in the libration of the ring which will be described below. The bond lengths and angles within the complex ion are given in Table IV. The interatomic distances outside the complex ion are shown in Table V.[9c] Possible hydrogen bonds are listed in Table VI; however there is no hydrogen bond between the neighboring complex ion.

Figure 3 shows an ORTEP drawing of the complex ion and the numbering scheme of the atoms. The cobalt atom is octahedrally surrounded by four nitrogen atoms of the quadridentate ligand and the two oxygen atoms of the acac ring.

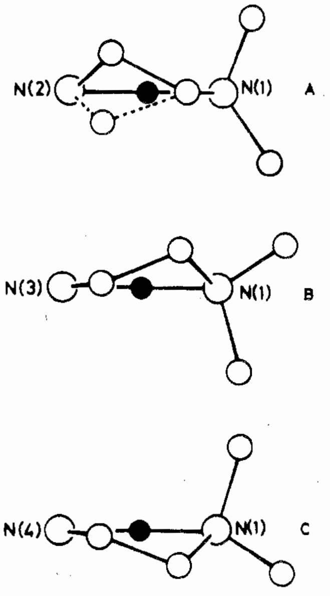

Figure 4. Conformation of the three rings of tren.

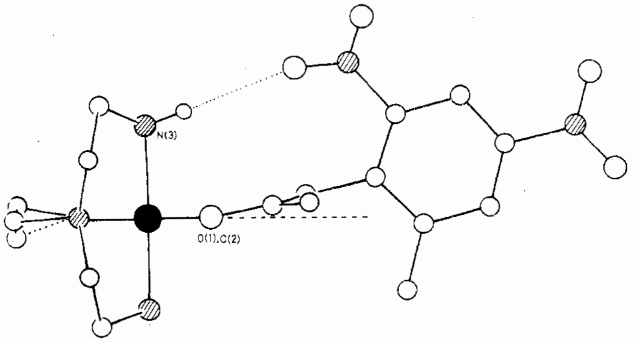

Figure 5. A projection along the line of O(1), O(2) of the acac ring.

Since the primary amino groups are constrained to approach the tertiary amino nitrogen atom, the angles subtended at the cobalt atom by the three chelate rings are compressed to an average angle of 86.9 (3)°. This value is, however, slightly larger than that of corresponding chelate rings in [Co(gly)-tren]$^{2+}$.[13] The bond length of Co–N(2), 1.933 (6) Å, is shorter than other Co–N bonds. This shortening of Co–N(2) is probably due to constraints of tren. Such shortening is also observed for the secondary nitrogen atoms in some other complexes.[14] The three five-membered chelate rings of tren adopt an envelope conformation (see Figure 4). Rings B and C are in plane along the *c* axis and enantiomeric to each other. Ring A is nearly perpendicular to rings B and C; it has a conformational disorder, δ conformation being predominant in the ratio of 4 to 1: this conformation is appropriate to form hydrogen bonds between the primary amino nitrogen and bromide ions. Other bond distances and angles are normal.

A projection along the line through O(1) and O(2) is shown in Figure 5. The six-membered acac ring takes up a flattened boat form as is the case in bis(3-phenylpentane-2,4-dionato)copper(III).[15] Normal values are observed for bond lengths and angles. The dihedral angle between O(1)–Co–O(2) and O(1)–C(8)C(10)–O(2) planes is 11.0°; that between O(1)–

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C(8)C(10)–O(2) and C(8)–C(9)–C(10) is 5.0°. The pivot bond C(9)–C(12) bends toward the opposite side of the ortho nitro group and has a tilt angle of 2.6° to the C(8)–C(9)–C(10) plane. All these bending directions are almost perpendicular to the plane of O(1)–Co–O(2). Thermal parameters of the acac ring show slight out-of-plane vibrations of the ring. The aromatic ring is nearly perpendicular to the acac ring. Inspection of the thermal parameters shows that the aromatic ring librates around the pivot bond. The geometry is normal except for that of the ortho nitro group. The group is disordered with a ratio of 50:50.

Since two chelate rings of tren, B and C, are enantiomeric to each other and only ring A contributes to the optical activity, the environment around the cobalt atom is apparently almost symmetric as far as the acac oxygen atoms and tren are concerned. In spite of such structure, the present complex shows significantly large optical rotation. If the above geometry of the complex ion still stands for the average conformation in an aqueous solution, the bent structure of the acac ring should be taken into account for the model of the present series. Not only the disposition of the ortho nitro group and C(18) methyl group but also the bent structure and the disposition of the aromatic ring break the symmetry of coordination sphere. The possible interaction between the ortho nitro group and the amino group may also contribute. These dissymmetric effects seem to be comparable to the dissymmetry of optically active complexes whose activity arises from the chirality within the coordination sphere.

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Registry No. $[(-)_{589}$-3-(6-Methyl-2,4-dinitrophenyl)pentane-2,4-dionato][tris(2-aminoethyl)amine]cobalt(III) dibromide dihydrate, 74397-72-1; 3-(6-methyl-2,4-dinitrophenyl)pentane-2,4-dione, 74397-55-0; 1-chloro-6-methyl-2,4-dinitrobenzene, 18905-50-5; 1-fluoro-6-methyl-2,4-dinitrobenzene, 348-97-0; sodium acetylacetonate, 15435-71-9.

Supplementary Material Available: Tables III and V, showing observed and calculated intensity relations between some *hkl* and *hkl* reflections and relevant interatomic distances less than 3.5 Å outside the complex ions, and a table of observed and calculated structure amplitudes (19 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale ed Inorganica dell'Università, Laboratorio CNR, 50132 Firenze, Italy,
and the Istituto di Chimica Generale della Factoltà di Farmacia, Università di Firenze, 50121 Firenze, Italy

Crystal and Molecular Structure and ESR Spectra of a Dimeric Dialkoxo-Bridged Five-Coordinate Copper(II) Complex

LUCIA BANCI, ALESSANDRO BENCINI, PAOLO DAPPORTO, ANDREA DEI,[1] and DANTE GATTESCHI*

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The crystal and molecular structure of bis(*N,N*-bis(2-(diethylamino)ethyl)-2-hydroxyethylamino-*O*)dicopper(II) diperchlorate has been determined by X-ray diffractometry data. The crystals are monoclinic, of space group $P2_1/n$, with cell dimensions $a = 9.349$ (2) Å, $b = 17.676$ (4) Å, $c = 11.720$ (3) Å, and $\beta = 93.02$ (2)°. The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional R factor of 0.055 over the 1367 independent observed reflections. The structure consists of dinuclear $[Cu_2(bdhe)_2]^{2+}$ cations, which possess a center of symmetry, and of perchlorate anions. The copper(II) ions achieve five-coordination by sharing the oxygen atoms of the ligand. The arrangement of the ligands around the metal ion is intermediate between a trigonal-bipyramidal and a square-pyramidal model. The copper(II)–copper(II) distance is 3.044 (2) Å. Single-crystal ESR spectra of the zinc(II)-doped complex were recorded in order to relate the structural data to the electronic properties. The anisotropic g values and their principal directions were reproduced through an angular overlap (AO) model. The magnetic susceptibility data are discussed within the same formalism.

Introduction

The attempt to relate the magnetic coupling observed in dinuclear complexes with the structural features of the bridged moieties is one of the main research topics of the last few years.[2-6] The problem has been tackled both theoretically[7-11] and experimentally,[12-14] and several useful correlations are now available.

Two of us recently reported the spectral and magnetic properties of a series of dinuclear 3d metal complexes with *N,N*-bis(2-(diethylamino)ethyl)-2-hydroxyethylamine (bdheH), $[M_2(bdhe)_2](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn),[15] and found a large variation in the following values of the magnetic coupling constant J (defined through the Hamiltonian $H = -J(S_1 \cdot S_2)$): -495 cm^{-1} for the copper(II), -35 cm^{-1} for the nickel(II), -17 cm^{-1} for the cobalt(II) complex, and smaller values for the iron(II) and manganese(II) derivatives. The structure of the nickel(II) complex is available,[16] showing that the metal ions are in a distorted trigonal-bipy-

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* To whom correspondence should be addressed at the Istituto di Chimica Generale ed Inorganica dell'Università.

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