particular higher energy conformation, brought about by the twisting of the molecule, in which two hydrogens with a small positive charge, both in the vicinity of the metals, and at near-bonding distances, homolytic cleavage of the hydrogens will occur and molecular hydrogen will be liberated. The rapid proton exchange between the metal and rings and around the ring system, as suggested by the present calculations, is consistent with the observation[15] that when [1.1]ferrocenophane is dissolved in fully deuterated acid $BF_3 \cdot D_2O$, an isotopic mixture of composition 10:3:1 H_2:HD:D_2 is liberated.

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Registry No. [1.1]Ferrocenophane, 1294-39-9.

Contribution from the Department of Chemistry,
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Structure and Properties of a Cobalt(III) Complex with a Branched Cyclic Tetraamine Ligand, (6-Methyl-6-(4-amino-2-azabutyl)-1,4-diazacycloheptane)(ethylenediamine)cobalt(III) Perchlorate

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The preparation and properties of a cobalt(III) complex with a new branched cyclic tetraamine ligand, $[Co(L)(en)](ClO_4)_3$, are described, where L is 6-methyl-6-(4-amino-2-azabutyl)-1,4-diazacycloheptane and en is ethylenediamine. The structure of the red complex $[Co(C_9H_{22}N_4)(C_2H_8N_2)](ClO_4)_3$ has been determined by single-crystal X-ray diffraction techniques ($R = 0.0462$, orthorhombic crystals, space group *Pbca* with $a = 14.059$ (3) Å, $b = 15.319$ (5) Å, $c = 20.497$ (6) Å, and $Z = 8$). The cobalt(III) ion is surrounded by six nitrogen atoms, four from L and two from en. The N–Co–N angle subtended by the two nitrogens of the 1,4-diazacycloheptane moiety is unusually small (76.4 (1)°). While the Co–N bonds trans to these two nitrogens have normal lengths, the other four Co–N bonds are elongated due to steric strain in the L ligand and the steric repulsion between the hydrogens of L and en. The correlation between the λ_{max} values in absorption spectra and the average Co–N lengths of $[Co(N)_6]$ complexes has been found and used to explain the large red shift in the absorption spectrum of this complex.

Introduction

In a recent series of papers,[1,2] we have been studying the stereoselective association in solution between trigonal $[Co(N)_6]^{3+}$ complexes and *d*-tartrate or bis(μ-*d*-tartrato)diantimonate(III) ion. In that work, we have improved the synthetic method of $[Co(sen)]^{3+}$ for large-scale synthesis, where sen is 1,1,1-tris(4-amino-2-azabutyl)ethane. During the synthesis of $[Co(sen)]^{3+}$, a red crystalline compound was isolated in a yield comparable to that of $[Co(sen)]^{3+}$. The visible absorption spectrum of this compound in water appeared to be consistent with the *cis*-$[Co(O)_2(N)_4]$ chromophore. The chemical analysis was not, however, consistent with any complex involving such a chromophore. The proton NMR spectrum in deuterium oxide was very complex at 60 MHz and was not very helpful in deducing the structure of the compound. Thus, the compound was subjected to the structure determination by single-crystal X-ray diffraction, and it is disclosed that the compound was of the $[Co(N)_6]$ type and contained a novel branched cyclic tetraamine ligand, 6-methyl-6-(4-amino-2-azabutyl)-1,4-diazacycloheptane (L). This paper describes the preparation, spectral characteristics, and structure of the complex, as well as a discussion on the origin of the large red shift in the absorption spectrum of this compound.

Experimental Section

Preparation of $[Co(sen)]^{3+}$ and $[Co(L)(en)]^{3+}$. 1,1,1-Tris(hydroxymethyl)ethane was tosylated in pyridine after Heinz and Burkhardt.[3] The tritosylate (100 g) was refluxed with a large excess of anhydrous ethylenediamine (en) (500 g) for 72 h out of contact with atmospheric moisture and carbon dioxide. Excess en was removed by a rotary evaporator, a solution of sodium hydroxide (240 g) in water (400 mL) was added to the viscous yellow residue, and this mixture then was extracted three times with pyridine (1 L). The extracts were rotary evaporated to give a viscous yellow oil, to which 300 mL of ethanol was added. The mixture was suction filtered to remove *p*-toluenesulfonic acid salts, and this ethanolic solution of crude sen (containing also L and en) was used directly in the subsequent reaction.

Sixty grams of *trans*-$[CoCl_2(py)_4]Cl$[4] (py = pyridine) in 1 L of warm methanol was added, with stirring, to the above ethanolic solution. The orange precipitate of $[Co(sen)]Cl_3$ that was formed was suction filtered, washed with ethanol and ether, and recrystallized from warm water, yielding 35 g of analytically pure $[Co(sen)]Cl_3$. The overall yield based on the starting material 1,1,1-tris(hydroxymethyl)ethane was about 60%. To the dark red-brown filtrate was added a further amount (30 g) of *trans*-$[CoCl_2(py)_4]Cl$ with mechanical stirring, and the solution was concentrated by a rotary evaporator, yielding a red precipitate. This was the chloride salt of $[Co(L)(en)]^{3+}$, which was collected by filtration. Because the chloride salt was rather hygroscopic, it was transformed into the perchlorate salt by using an anion-exchange column of QAE-Sephadex A-25 (perchlorate form). The effluent was concentrated on a rotary evaporator, and the precipitate was collected by filtration. The perchlorate salt was recrystallized from warm water, and its yield was about 20 g (19% based on the tritosylate). Anal. Calcd for $[Co(C_{11}H_{30}N_6)](ClO_4)_3$: C, 21.89; H, 5.01; N, 13.92. Found: C, 21.90; H, 5.31; N, 14.00.

Measurements. Proton magnetic resonance spectra were obtained on a JEOL JNM PMX-60 spectrometer at 60 MHz and 37 °C, with an internal standard of sodium 4,4-dimethyl-4-sila-1-pentanesulfonate (DSS). Electronic absorption spectra were obtained on a Shimadzu UV-240 double-beam recording spectrophotometer at ambient temperature.

The optical resolution of $[Co(L)(en)]^{3+}$ was effected by reversed-phase ion-pair chromatography with 0.01 M potassium bis(μ-*d*-tartrato)diantimonate(III) as the ion-pairing reagent.[5] The column packing was LS-410 ODS.SIL. (Toyo Soda Manufacturing

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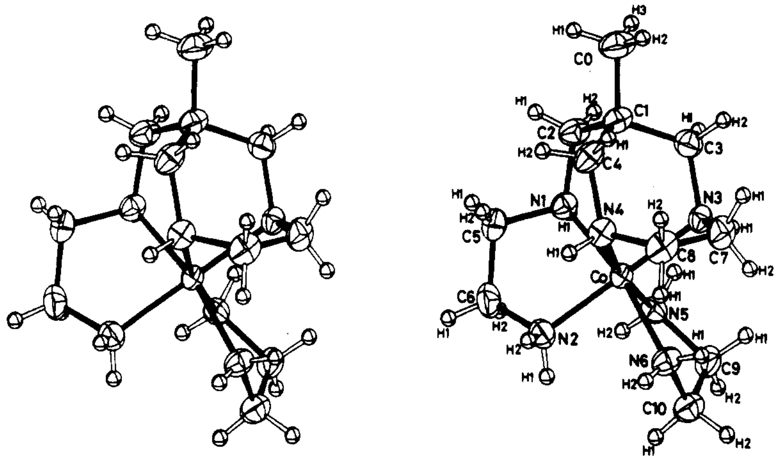

Figure 1. ORTEP diagram of the cation with 50% thermal ellipsoids. The Δ cation is shown.

Co., Ltd.), which carries *n*-octadecyl groups covalently bonded to the surface of silica gel. The chromatographic apparatus was the same as in previous studies.[5] Experimental details including the optical resolution of other $[Co(N)_6]^{3+}$ ions will be reported separately.[6] The optically active compound was not isolated in this work, and the complex concentration was determined spectrophotometrically. The circular dichroism (CD) spectra were run on a JASCO J-40CS recording spectropolarimeter.

Collection of the X-ray Diffraction Data for $[Co(L)(en)](ClO_4)_3$. A red crystal of $[Co(C_9H_{22}N_4)(C_2H_8N_2)](ClO_4)_3$ with the dimensions of 0.56 × 0.63 × 0.68 mm was used for the data collection. The determination of cell constants and the intensity data collection were carried out at 20 °C on a Syntex R3 automated four-circle diffractometer with Mo Kα radiation made monochromatic by a graphite plate ($\lambda = 0.1069$ Å). The cell constants, determined by a least-squares method using 15 independent reflections with $21.0° < 2\theta < 27.0°$, were $a = 14.059$ (3) Å, $b = 15.319$ (5) Å, $c = 20.497$ (6) Å, and $V = 4413.2$ (6) Å^3. The space group was determined as *Pbca* (D_{2h}^{15}, No. 61) from the systematic absences for $h0l$ ($l = 2n + 1$), $hk0$ ($h = 2n + 1$), and $0kl$ ($k = 2n + 1$). The measured density of 1.82 g cm^{-3} obtained by the flotation method using a $CHCl_3$–$CHBr_3$ mixed solution agreed well with the calculated value of 1.817 g cm^{-3} for $Z = 8$. The intensity data were measured for an octant $(+h,+k,+l)$ up to $2\theta = 55°$ by using the ω-scan technique with a scan speed of 3–30°/min (50 kV, 20 mA). Three reference reflections monitored after every cycle of 197 measurements showed no significant variation in intensity during the data collection. Out of 5066 reflections measured, 4290 reflections with $|F_o| > 3\sigma(|F_o|)$ were selected and used for the structure determination. They were corrected for Lorentz–polarization factors, but no absorption correction was applied since the linear absorption coefficient, μ(Mo Kα) = 12.5 cm^{-1}, was low.

Structure Determination and Refinement. The position of the Co atom was located by using the results of MULTAN direct-methods analysis (MULTAN 78[7]). All other computations were carried out by using the Universal Crystallographic Computation Program System, UNICS III.[8] Subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. After all the non-hydrogen atoms were refined isotropically, a series of refinements using anisotropic thermal parameters for all non-hydrogen atoms reduced an R value, $\sum(|F_o| - |F_c|)/\sum|F_o|$, to 0.0618 and an R_w value, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, to 0.0692. The weighting scheme used was as follows: for $|F_o| < 5$, $w = 0.7$; for $5 < |F_o| < 150$, $w = 1.0$; for $|F_o| < 150$, $w = (150.0/|F_o|)^2$. All the hydrogen atoms were located from subsequent difference Fourier maps. All atoms were further refined, non-hydrogen atoms anisotropically and hydrogen atoms isotropically. A final refinement converged R to 0.0462 and R_w to 0.0472. The largest residuals, 0.9 e/Å^3, in the final difference Fourier map are located near the oxygen atoms of the three perchlorate groups. All the atomic scattering factors were taken from Cromer and Waber.[9a]

Table I. Atomic Coordinates for Non-Hydrogen Atoms (×10^4)

atom	*x*	*y*	*z*
Co	5516 (0)	2504 (0)	1101 (0)
ClA	4124 (1)	4071 (1)	−917 (0)
ClB	6459 (1)	−1035 (1)	957 (1)
ClC	2808 (1)	731 (1)	1320 (1)
OA1	4296 (2)	4913 (2)	−624 (2)
OA2	3238 (2)	3754 (2)	−677 (2)
OA3	4855 (2)	3490 (2)	−715 (2)
OA4	4091 (3)	4153 (2)	−1598 (2)
OB1	7398 (2)	−727 (2)	1053 (2)
OB2	5904 (3)	−425 (2)	620 (2)
OB3	6518 (3)	−1812 (2)	596 (3)
OB4	6042 (3)	−1159 (4)	1563 (2)
OC1	3005 (3)	1613 (2)	1488 (2)
OC2	3620 (4)	384 (3)	1027 (3)
OC3	2561 (6)	274 (3)	1865 (2)
OC4	2054 (4)	712 (4)	890 (4)
N1	5337 (2)	3661 (2)	1532 (1)
N2	4262 (2)	2764 (2)	708 (1)
N3	6710 (2)	2126 (2)	1545 (1)
N4	5049 (2)	1875 (2)	1894 (1)
N5	6180 (2)	3080 (2)	375 (1)
N6	5524 (2)	1463 (2)	515 (1)
C0	6371 (3)	3205 (3)	3202 (2)
C1	6081 (3)	2993 (2)	2504 (2)
C2	5758 (3)	3829 (2)	2183 (2)
C3	6952 (3)	2645 (2)	2140 (2)
C4	5253 (3)	2338 (2)	2527 (2)
C5	4305 (3)	3871 (2)	1522 (2)
C6	3941 (3)	3666 (3)	860 (2)
C7	6583 (3)	1185 (2)	1736 (2)
C8	5553 (3)	1019 (2)	1892 (2)
C9	6588 (3)	2410 (3)	−69 (2)
C10	5859 (3)	1707 (2)	−146 (2)

The anomalous dispersion coefficients of Cromer and Liberman[9b] were used for Co and Cl. The final atomic coordinates for non-hydrogen and hydrogen atoms and the final thermal parameters are given in Tables I, II, and III, respectively, according to the atom labels of Figure 1 (Tables II and III are supplementary material). All the computations including ORTEP drawings[10] were carried out by a HITAC M-200 computer at the Hiroshima University Information Processing Center. A table of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

Preparation of $[Co(sen)]^{3+}$ and $[Co(L)(en)]^{3+}$. The synthesis of $[Co(sen)]^{3+}$ reported previously[11] is very tedious and

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time-consuming, and the yield is rather low. This point was noted previously by several workers.[12,13] The present method of synthesis involves the tosylation of the starting material 1,1,1-tris(hydroxymethyl)ethane, followed by refluxing the tritosylated compound with a large excess of en. Evaporation of excess en and extraction with pyridine yield crude sen, which also contains the cyclization product L and some en. It was rather difficult to remove completely the residual en because crude sen and L are very viscous. The crude sen is then mixed with *trans*-$[CoCl_2(py)_4]Cl$ in warm methanol, yielding a yellow precipitate of $[Co(sen)]Cl_3$. Filtration of $[Co(sen)]Cl_3$ gives a dark red-brown solution, from which a red compound precipitates by addition of a further amount of *trans*-$[CoCl_2(py)_4]Cl$ and evaporation of the solvent.

The synthetic method $[Co(sen)]Cl_3$ employed here is essentially similar to the recently reported method of Geue and Searle,[13] which involves the toluenesulfonation of the starting material and the air oxidation of the methanol solution containing Co^{2+} and chromatographically purified sen. The yield is also similar, but the present method seems to be convenient and especially suited for large-scale synthesis of both $[Co(sen)]^{3+}$ and $[Co(L)(en)]^{3+}$.

The production of L in the synthesis of sen was noted by Geue and Searle.[13] This L ligand might be formed by an intramolecular nucleophilic attack of the NH_2 group of a 4-amino-2-azabutyl moiety, which is formed first, on the carbon atom of the neighboring $-CH_2OTs$ function (Ts = $CH_3C_6H_4SO_2$). Since the yield of L was comparable to that of sen despite the use of a large excess of en over the tosylate, this intramolecular attack can be considered to proceed very easily and compete effectively with the intermolecular one.

Properties of $[Co(L)(en)]^{3+}$. The UV/vis spectrum of $[Co(L)(en)](ClO_4)_3$ in water has band peaks at 496 nm (ϵ 155), 356 nm (ϵ 164), and 231 nm (ϵ 20050). The peak positions are red shifted from those of the relevant $[Co(N)_6]^{3+}$ complexes, e.g., 469 nm (ϵ 87) and 340 nm (ϵ 79) for $[Co(en)_3]^{3+}$ and 467 nm (ϵ 113) and 340 nm (ϵ 103) for $[Co(sen)]^{3+}$,[12b] and are rather close to those of the *cis*-$[Co(N)_4(O)_2]$ chromophore, e.g., 495 nm (ϵ 71) and 356 nm (ϵ 66) for *cis*-$[Co(en)_2(OH_2)_2]^{3+}$.[14] The unusually high intensity and low energy of the $^1T_{1g}$ bands in the absorption spectrum may be attributed to a steric strain of this complex.[15] This inference seems to be substantiated by the structure determination (see below).

The complex could be resolved optically by reversed-phase ion-pair chromatography with potassium bis(μ-*d*-tartrato)diantimonate(III) as the ion-pairing reagent.[5,6] The later eluted enantiomer, which is favored by the ion-pairing reagent, exhibited a single positive CD band centered at 518 nm with $\Delta\epsilon = +2.27$ in the $^1T_{1g}$ region, and this enantiomer may be assigned a Λ absolute configuration by comparison with the CD spectra of other $[Co(N)_6]^{3+}$ complexes.[16] This assignment is consistent also with the elution order of enantiomers of most $[Co(N)_6]^{3+}$ complexes with five-membered chelate rings obtained by this chromatographic technique.[6]

The proton NMR spectrum of $[Co(L)(en)](ClO_4)_3$ in deuterium oxide at 60 MHz consists of a methyl singlet at δ 1.00 and a complex multiplet ranging from δ 2.167 to δ 3.70, indicating only the presence of a tris(methylene)ethane capping group. It was difficult to analyze the multiplet to extract any further structural information.

Table IV. Intramolecular Bond Distances (Å) with Least-Squares Esd's in Parentheses

Co–N1	1.997 (3)	Co–N2	1.979 (3)
Co–N3	1.995 (3)	Co–N4	2.000 (3)
Co–N5	1.966 (3)	Co–N6	1.996 (3)
ClA–OA1	1.444 (3)	ClA–OA2	1.424 (4)
ClA–OA3	1.421 (4)	ClA–OA4	1.401 (4)
ClB–OB1	1.416 (4)	ClB–OB2	1.399 (4)
ClB–OB3	1.405 (6)	ClB–OB4	1.387 (6)
ClC–OC1	1.422 (5)	ClC–OC2	1.395 (6)
ClC–OC3	1.363 (8)	ClC–OC4	1.378 (8)
N1–C2	1.481 (5)	N1–C5	1.487 (5)
N2–C6	1.486 (5)	N3–C3	1.494 (4)
N3–C7	1.504 (5)	N4–C4	1.506 (5)
N4–C8	1.491 (5)	N5–C9	1.486 (5)
N6–C10	1.484 (5)	C0–C1	1.522 (6)
C1–C2	1.510 (5)	C1–C3	1.530 (5)
C1–C4	1.537 (5)	C5–C6	1.485 (6)
C7–C8	1.506 (6)	C9–C10	1.495 (6)

Table V. Intramolecular Bond Angles (deg) with Least-Squares Esd's in Parentheses

N1–Co–N2	83.6 (1)	N3–Co–N4	76.4 (1)
N5–Co–N6	84.3 (1)	N1–Co–N6	167.5 (1)
N2–Co–N3	173.5 (1)	N4–Co–N5	170.8 (1)
Co–N1–C2	120.1 (2)	Co–N1–C5	108.0 (2)
C2–N1–C5	111.5 (3)	Co–N2–C6	111.9 (2)
Co–N3–C3	114.2 (2)	Co–N3–C7	107.3 (2)
C3–N3–C7	108.9 (3)	Co–N4–C4	114.3 (2)
Co–N4–C8	105.4 (2)	C4–N4–C8	109.0 (3)
Co–N5–C9	109.6 (2)	Co–N6–C10	110.5 (2)
C0–C1–C2	108.0 (3)	C0–C1–C3	108.6 (3)
C0–C1–C4	108.3 (3)	C2–C1–C3	108.8 (3)
C2–C1–C4	109.8 (3)	C3–C1–C4	113.2 (3)
N1–C2–C1	111.5 (3)	N3–C3–C1	113.7 (3)
N4–C4–C1	115.2 (3)	N1–C5–C6	107.7 (3)
N2–C6–C5	106.4 (3)	N3–C7–C8	109.4 (3)
N4–C8–C7	108.0 (3)	N5–C9–C10	107.4 (3)
N6–C10–C9	107.6 (3)		

Structure of $[Co(L)(en)](ClO_4)_3$. Intramolecular bond distances and bond angles, with estimated standard deviations, are listed in Tables IV and V. An ORTEP drawing of the cation with atom labels is shown in Figure 1 as a stereopair. In the figure, the thermal ellipsoids have been drawn to include 50% of the probability distribution. In the crystal some of the amine hydrogens are hydrogen bonded to perchlorate oxygens, and important hydrogen bonds are listed in Table VI (supplementary material).

The cobalt(III) ion is surrounded by six nitrogen atoms, four from the branched cyclic tetraamine ligand, 6-methyl-6-(4-amino-2-azabutyl)-1,4-diazacycloheptane (L), and two from en. The chelate bite angles N1–Co–N2 and N5–Co–N6 are quite normal for five-membered chelate rings, but the N3–Co–N4 angle is rather small (76.4 (1)°). Usually, the chelate bite angle of en ligand or the en moiety has been reported to range from 84 to 86°.[17,18] The three Co–N–C angles involving the nitrogen atoms attached to the tris(methylene)ethane cap, namely, Co–N4–C4, Co–N1–C2, and Co–N3–C3, are all significantly distorted from the tetrahedral value, the deviation being largest for Co–N1–C2 of 120.1 (2)°. The 1,4-diazacycloheptane moiety of L assumes a unique and rather strained conformation. The dihedral angles C8–N4–C4–C1, C7–N3–C3–C1, C4–N4–C8–C7, and C3–N3–C7–C8 are 95.1 (3), 88.8 (3), 78.4 (3), and 91.8 (3)°, respectively. The N3–

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C7–C8–N4 dihedral angle is 8.0 (4)°, indicating that this "ethylenediamine" chelate is almost flattened, and the hydrogens H1(C7), H2(C8) and H2(C7), H1(C8) are, respectively, almost eclipsed. These conformational characteristics produce several nonbonded interactions between hydrogens; e.g., the H1(C4)···H2(C8) and H2(C3)···H1(C7) distances are 2.06 (5) and 2.06 (6) Å, respectively. Also, the N3–C3–C1, C3–C1–C4, and C1–C4–N4 angles deviate from the tetrahedral value. As a result, the upper half of the complex cation suffers from a severe steric strain, which results, of course, from the cyclic and tetradentate nature of the L ligand.

While Co–N5 and Co–N2 bond lengths are normal, the other Co–N bond distances are somewhat longer (average 1.997 (2) Å) than the normal value. For comparison, the average Co–N bond lengths in Λ-$[Co(sen)]Cl(d\text{-}C_4H_4O_6)\cdot 6H_2O$[17] and Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$[18] are 1.971 (6) and 1.964 (3) Å, respectively. The elongation of the Co–N3, Co–N4, and Co–N1 bonds seems to arise from the highly strained coordinated mode of L. The lengthening of the Co–N6 bond may be attributed to the nonbonded steric repulsion between H1(N6) and H2(C7) and/or H1(C8). The H1(N6)···H2(C7) and H1(N6)···H1(C8) distances are 2.07 (5) and 2.22 (5) Å, respectively, and these distances are comparable to the sum of van der Waals radii of hydrogen atoms.[19] Thus, it appears that only N2 and N5 atoms can coordinate to the cobalt without suffering from steric strain and nonbonded interaction.

Origin of the Red Shift in the Absorption Spectrum. From the structural features described above, we may consider two effects as probable causes of the red shift in the absorption spectrum: the steric strain as manifested in the N3–Co–N4 angle and the Co–N4–C4, Co–N1–C2, and Co–N3–C3 angles and the elongation of Co–N bonds as found in Co–N1, Co–N3, Co–N4, and Co–N6 bond lengths. A question then arises: Which of these two effects is more important and are both effects equally important in inducing the red shift? A survey of the available X-ray crystallographic and absorption data[17–42] on more than 20 $[Co(N)_6]^{3+}$ complexes that contain only amine ligands points to the existence of a correlation between the λ_{max} values of the lowest energy $^1T_{1g}$ transition and the average Co–N bond lengths (Figure 2) but not between λ_{max} values and the N–Co–N angles (though the angles change over a very limited range, 84.0–94.5°). In the formalism of simple crystal field theory, the λ_{max} value is linearly related to the sixth power of the metal-to-ligand bond length. Therefore, the λ_{max} values are plotted in Figure 2 against r^6 rather than r, where r is the average Co–N length. Since the Co–N length might change depending upon the counteranion, only one data point for one particular complex cation, which is the average for several complexes containing that cation, is plotted. Thus, the data point for $[Co(en)_3]^{3+}$ (entry 1 in Figure 2), for example, is the average for three compounds, Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$,[18] Λ-$[Co(en)_3]Cl_3\cdot H_2O$,[20] and $[Co(en)_3]_2(HPO_4)_3\cdot 9H_2O$.[21] In Figure 2, standard deviations in Co–N

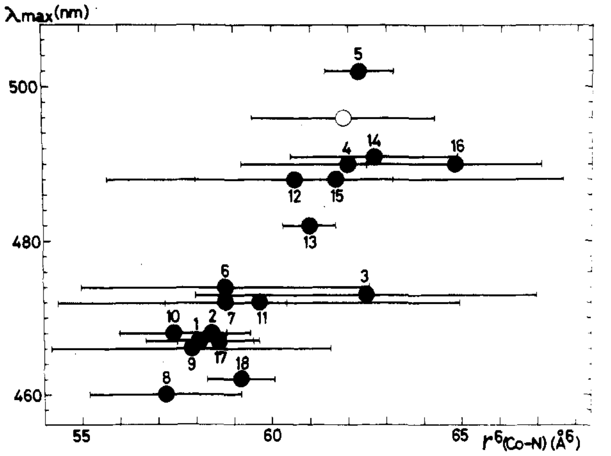

Figure 2. λ_{max} values vs. r^6 for $[Co(N)_6]^{3+}$ complexes, where r is the average Co–N bond length. Entry numbers refer to the following complexes: 1, average of Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$,[18] Λ-$[Co(en)_3]Cl_3\cdot H_2O$,[20] and $[Co(en)_3]^2(HPO_4)_3\cdot 9H_2O$;[21] 2, average of Δ-*lel*$_3$-$[Co(R\text{-}pn)_3]Br_3$,[22] Λ-*fac*-*ob*$_3$-$[Co(R\text{-}pn)_3][Co(CN)_6]\cdot 2H_2O$,[23] and Δ-$[Co(l\text{-}pn)_3]$-Λ-$[Cr(mal)_3]\cdot 3H_2O$;[24] 3, average of Λ-$[Co(d\text{-}chxn)_3]Cl_3\cdot 5H_2O$,[25] Λ-*lel*$_2$*ob*-$[Co(S,S\text{-}chxn)_2(R,R\text{-}chxn)]Cl_3\cdot 5H_2O$,[26] and Λ-*ob*$_3$-$[Co(l\text{-}chxn)_3]Cl_3\cdot H_2O$;[27] 4, average of Λ-$[Co(tn)_3]Cl_3\cdot H_2O$[28] and Λ-$[Co(tn)_3]Br_3\cdot H_2O$;[29] 5, Δ-$[Co(tmd)_3]Br_3$;[30] 6, Λ-$[Co(en)_2(tn)]Br_3$;[31] 7, $\Delta\lambda\lambda$-$[Co(tame)_2]Cl(d\text{-}C_4H_4O_6)\cdot H_2O$;[32] 8, *s*-*fac*-$[Co(dien)_2]Br_3$;[33] 9, *mer*-$[Co(dien)_2]Br_3\cdot 1.6H_2O$;[34] 10, *uns*-*fac*-$[Co(dien)_2][Co(CN)_6]\cdot 2H_2O$;[35] 11, $\Lambda\Lambda\Lambda\Delta$-$[Co(linpen)][Co(CN)_6]\cdot 3H_2O$;[36] 12, $\Lambda\Delta\Lambda$-$[Co(penten)][Co(CN)_6]\cdot 2H_2O$;[37] 13, Δ-$[Co(R,R\text{-}ptn)_3]Cl_3\cdot 2H_2O$;[38] 14, Λ-*fac*-$[Co(S,S\text{-}ptn)_3][Co(CN)_6]\cdot 5H_2O$;[39] 15, Λ-$[Co(R,R\text{-}ptn)_3]Cl_3\cdot H_2O$;[40] 16, Λ-$[Co(S,S\text{-}cptn)_3]Cl_3\cdot 4H_2O$;[41] 17, Λ-$[Co(sen)]Cl(d\text{-}C_4H_4O_6)\cdot 6H_2O$;[17] 18, $(-)_{589}$-$[Co(R\text{-}2\text{-}Me\text{-}tacn)_2]I_3\cdot 5H_2O$.[42] Abbreviations: pn = 1,2-propanediamine, mal = malonate, chxn = *trans*-1,2-cyclohexanediamine, tn = 1,3-propanediamine, tmd = 1,4-butanediamine, tame = 1,1,1-tris(2-aminoethyl)ethane, dien = diethylenetriamine, linpen = linear pentaethylenehexamine, penten = *N*,*N*,*N'*,*N'*-tetrakis(2-aminoethyl)ethylenediamine, ptn = 2,4-pentanediamine, cptn = *trans*-1,2-cyclopentanediamine, 2-Me-tacn = 2-methyl-1,4,7-triazacyclononane.

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lengths are indicated by horizontal bars. Within these experimental uncertainties, a correlation of the form

$$\lambda_{max}\ (\mathrm{nm}) = (4.83 \pm 0.03)r^6\ (\text{Å}^6) + (187 \pm 2)$$

seems to hold (correlation coefficient = 0.824). In Figure 2 are plotted the data points not only for $[\mathrm{Co(diamine)_3}]^{3+}$ but also for complexes containing secondary (entries 8–11, 17, and 18) and tertiary (entry 12) amines. Thus, it is very satisfactory to find the data point for $[\mathrm{Co(L)(en)}]^{3+}$ (an open circle in Figure 2) directly on the suggested correlation region.

In summary, the following conclusions may be drawn. Since an N–Co–N angle as small as 76.4° has not been reported to date, the effect of the chelate bite angle on the position of the absorption maximum cannot be properly assessed. Also, the problem of unusually high absorption intensity is not resolved. Figure 2 seems, however, to suggest strongly that the main cause for the red shift of the present complex lies in the relatively long Co–N bond lengths.

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Registry No. en, 107-15-3; $[\mathrm{Co(L)(en)}](\mathrm{ClO_4})_3$, 89907-10-8; Λ-$[\mathrm{Co(L)(en)}](\mathrm{ClO_4})_3$, 91199-93-8; $[\mathrm{Co(sen)}]\mathrm{Cl_3}$, 82796-46-1; *trans*-$[\mathrm{CoCl_2(py)_4}]\mathrm{Cl}$, 27883-34-7; Co, 7440-48-4; 1,1,1-tris(hydroxymethyl)ethane, 77-85-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, final atomic coordinates for hydrogen atoms with isotropic thermal parameters (Table II), final anisotropic thermal parameters for non-hydrogen atoms (Table III), and important hydrogen bond distances (Table VI) (23 pages). Ordering information is given on any current masthead page.

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Trinuclear Complexes of 1,3,5,7-Tetraketonates. Synthesis, Molecular Structure, Absorption Spectra, and Electrochemistry of Several Bis[1,7-diphenyl-1,3,5,7-heptanetetronato(3–)]bis[dioxouranium(VI)]metal(II)–4-Pyridine Complexes

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Several heterotrinuclear complexes have been prepared with the ligand 1,7-diphenyl-1,3,5,7-heptanetetrone. Two $\mathrm{UO_2}^{2+}$ ions occupy the terminal coordination positions in the molecules, and a divalent transition-metal ion occupies the central position. Crystallization from pyridine yields compounds abbreviated as $\mathrm{(UO_2)_2M(DBAA)_2(py)_4 \cdot 2py}$, where M(II) = Zn, Cu, Ni, Co, Fe, Mn. The X-ray crystal structures of the compounds where M is Ni(II), Co(II), Fe(II), and Mn(II) are reported. The structures are isomorphous. All are in the monoclinic space group $P2_1/c$. There are two molecules in the unit cell of each. The lattice constants with esd's, arranged in the sequence *a*, *b*, *c* (all in Å), *β* (in degrees), and *V* (in Å^3), are as follows: 13.436 (3), 24.011 (6), 10.566 (2), 108.12 (1), 3236 (1), for M = Ni; 13.45 (2), 23.93 (3), 10.62 (1), 108.3 (1), 3245 (8), for M = Co; 13.475 (2), 23.778 (3), 10.718 (1), 108.85(1), 3250 (1), for M = Fe; 13.473 (6), 23.507 (12), 10.834 (4), 109.08 (3), 3243 (2), for M = Mn. Cyclic voltammetric studies show that the U(VI) ions undergo quasi-reversible one-electron reductions in dimethylformamide with a platinum-disk electrode. The two ions yield two well-formed CV waves in the scan rate range of 0.020–2.000 V/s with a separation of 0.17–0.26 V. The separation is dependent upon the identity of the intervening transition metal. Differential pulse polarography was also employed to determine the peak separation values. The results were used to calculate conproportionality constants for the series. The values vary from about 2×10^3 to 2×10^4 in regular fashion going from Fe to Zn. The UV–visible spectral properties are also discussed.

Introduction

The *β*-polyketones are an homologous series potentially capable of forming a homologous series of polynuclear metal complexes. As such, they furnish an unusual opportunity to investigate the effect on chemical and physical properties of systematically increasing the number of interacting metal ions per molecule. The simplest members of the series, the bis(1,3-diketonato)metal complexes, have been extremely well studied throughout the history of modern coordination chemistry. The second members, the bis(1,3,5-triketonato)dimetal complexes, however, have been known only for about the past 15 years.[1] The third members, the bis(1,3,5,7-tetraketonato)trimetal complexes, are virtually unstudied. Two initial communications from our laboratory[2,3] are the only reports of trinuclear complexes of this interesting class of ligands. The work reported herein represents the first structural characterization of trinuclear 1,3,5,7-tetraketonates and establishes their ability to form trinuclear molecular complexes in a manner analogous to that for the mono- and dinuclear complexes of the 1,3-di- and 1,3,5-triketonates.

Table I. Comparison between the Calculated and Observed Elemental Analyses for $[\mathrm{(UO_2)_2M(DBAA)_2(py)_4}]\cdot\mathrm{2py}$, $\mathrm{C_{68}H_{56}O_{12}N_6U_2M}$

element		M					
		Mn	Fe	Co	Ni	Cu	Zn
C	calcd	48.61	48.58	48.49	48.51	48.36	48.31
	obsd	48.56	48.50	48.23	48.35	47.80	48.66
H	calcd	3.36	3.36	3.35	3.35	3.34	3.34
	obsd	3.42	3.53	3.45	3.39	3.37	3.53
N	calcd	5.00	5.00	4.99	4.99	4.98	4.97
	obsd	4.93	5.03	4.98	4.97	4.77	5.14
U	calcd	28.33	28.32	28.27	28.27	28.19	28.16
	obsd	28.40	28.06	27.30	28.56	28.50	27.85
M	calcd	3.27	3.32	3.50	3.49	3.76	3.87
	obsd	3.13	3.13	3.48	3.52	3.80	3.86

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