CHEMISTRY LETTERS, pp. 349 - 352, 1984.

STRUCTURE OF (6-METHYL-6-(4-AMINO-2-AZA-BUTYL)-1,4-DIAZACYCLOHEPTANE)-(ETHYLENEDIAMINE)COBALT(III) PERCHLORATE AND CORRELATION BETWEEN Co-N BOND LENGTH AND POSITION OF ABSORPTION MAXIMUM IN $[Co(N)_6]$ COMPLEXES

Ushio SAKAGUCHI, Kanji TOMIOKA, and Hayami YONEDA*
Department of Chemistry, Faculty of Science, Hiroshima University,
Hiroshima 730

The structure of the title compound, $[Co(C_9H_{22}N_4)(C_2H_8N_2)]-(ClO_4)_3$, has been determined by X-ray techniques. The correlation between the λ_{max} values in the absorption spectra and the average Co-N lengths in $[Co(N)_6]$ complexes has been used to explain the large red-shift in the absorption spectrum of this compound.

Recently, we have been studying[1)] the stereoselective association between the d-tartrate or bis(μ-d-tartrato)diantimonate(III) ion and trigonal $[Co(N)_6]^{3+}$ complexes involving $[Co(sen)]^{3+}$, where sen is 1,1,1-tris(4-amino-2-aza-butyl)-ethane. During the synthesis of $[Co(sen)]^{3+}$,[2)] we isolated a red crystalline compound containing a novel ligand, 6-methyl-6-(4-amino-2-aza-butyl)-1,4-diazacycloheptane (L), and an ethylenediamine (en). Herein are described the structure of the compound, $[Co(L)(en)](ClO_4)_3$, and a discussion about the origin of the large red-shift in the absorption spectrum of this compound.

The preparation of $[Co(L)(en)](ClO_4)_3$ is outlined below. 1,1,1-Tris(hydroxymethyl)ethane was tosylated and the resulting tritosylate was refluxed with a large excess of en. Removal of excess en, extraction with pyridine, and evaporation of pyridine by a rotary evaporator yielded crude sen, which contained also the cyclization product (L) and some en. This crude sen was mixed with trans-$[CoCl_2(py)_4]Cl$ (py = pyridine)[3)] dissolved in warm methanol. An orange precipitate of $[Co(sen)]Cl_3$ was suction-filtered and to the dark red-brown filtrate was added a further amount of trans-$[CoCl_2(py)_4]Cl$. Concentration of this solution gave the precipitate of the chloride salt of $[Co(L)(en)]^{3+}$. Since the chloride salt was hygroscopic, the complex was isolated as the perchlorate salt. The yield of $[Co(L)(en)](ClO_4)_3$ was about 19% based on the tritosylate.

Table 1. Crystallographic Data

Crystal system	orthorhombic
Space group	P_{bca}(No. 61)
a/Å	14.059(3)
b/Å	15.319(5)
c/Å	20.497(6)
V/Å^3	4413.2(6)
d_{calcd}/g cm^{-3}	1.817
d_{obsd}/g cm^{-3}	1.82
Z	8
Color	red
Dimensions/mm	0.56x0.63x0.68
Diffractometer	Syntex R3
Radiation	Mo K_α(λ0.71069Å)
Monochromator	graphite
Mode	ω-scan
2θ range/deg.	0-55.0
Reflctns measd.	5066
Reflctns used	4290
R	0.0462
R_w	0.0472

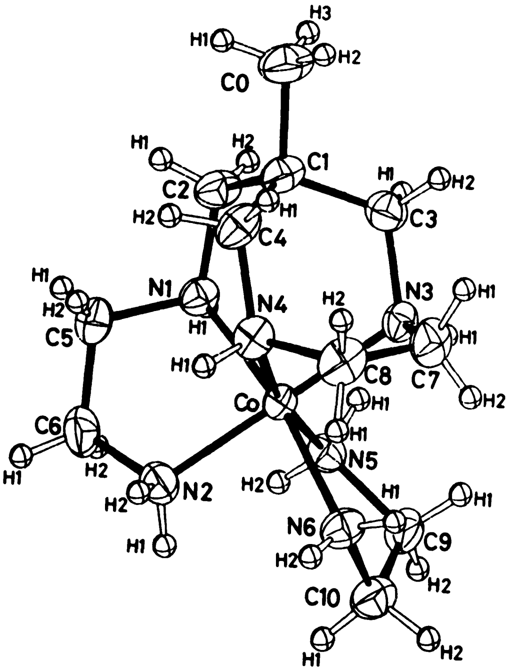

Fig. 1. ORTEP diagram of the cation with 50% thermal ellipsoids.

Crystallographic data of $[Co(L)(en)](ClO_4)_3$ are summarized in Table 1. The structure of the cation with atom labels is illustrated in Fig. 1. Anomalous features of the cation geometry are (i) the N3-Co-N4 angle is remarkably small (76.4(1)°), (ii) the Co-N4-C4, Co-N1-C2, and Co-N3-C3 angles (113.7(2)°, 120.1(2)°, 114.2(2)°, respectively) are distorted significantly from the tetrahedral value, (iii) the N3-C3-C1, C3-C1-C4, and C1-C4-N4 angles (113.7(3)°, 113.2(3)°, and 115.2(3)°, respectively) deviate also from the tetrahedral value, (iv) while the Co-N5 (1.966(3) Å) and Co-N2 (1.979(3) Å) bond lengths are normal, the other Co-N bond lengths (Co-N1, 1.997(3) Å; Co-N3, 1.995(3) Å; Co-N4, 2.000(3) Å; Co-N6, 1.996(3) Å) appear to be somewhat long, (v) H1(N6) suffers from a severe non-bonded interaction with H2(C7) and H1(C8), with distances 2.068(3) Å and 2.223(3) Å, respectively. All the other bond lengths and angles appear to be normal.

The electronic absorption spectrum of $[Co(L)(en)](ClO_4)_3$ in water has band peaks at 496(ε=155) and 356(164) nm. These peak positions are significantly red-shifted from those of the relevant $[Co(N)_6]^{3+}$ complexes, e.g., 469(87) and 340(79) nm for $[Co(en)_3]^{3+}$ and 467(113) and 340(103) nm for $[Co(sen)]^{3+}$.[4] Also, the absorption intensity may be noted to be rather high. The unusually high intensity and low energy of the $^1T_{1g}$ band in the absorption spectrum have been attributed to a steric strain.[5)] It appears, however, that the mechanism by which the strain brings about the high intensity and red-shift is not clear.

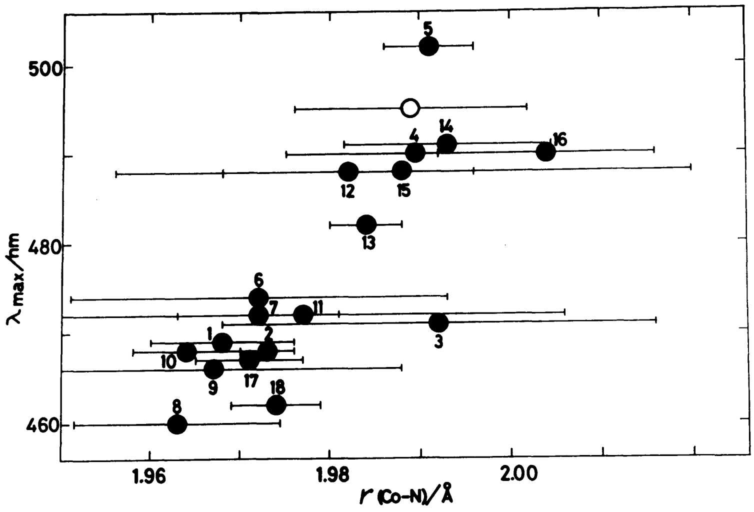

Fig. 2. The plots of λ_{max} values against average Co-N lengths for $[Co(N)_6]^{3+}$ complexes. Data are taken from Ref. 6. Entry numbers refer to the following complexes. 1: $[Co(en)_3]^{3+}$. 2: average of Δ-lel$_3$-$[Co(R\text{-}pn)_3]^{3+}$, Λ-fac-ob$_3$-$[Co(R\text{-}pn)_3]^{3+}$, and Δ-$[Co(l\text{-}pn)_3]^{3+}$. 3: average of Λ-$[Co(d\text{-}chxn)_3]^{3+}$, Λ-lel$_2$ob-$[Co(S,S\text{-}chxn)_2(R,R\text{-}chxn)]^{3+}$, and Λ-ob$_3$-$[Co(l\text{-}chxn)_3]^{3+}$. 4: $[Co(tn)_3]^{3+}$. 5: $[Co(tmd)_3]^{3+}$. 6: $[Co(en)_2(tn)]^{3+}$. 7: $[Co(tame)_2]^{3+}$. 8: s-fac-$[Co(dien)_2]^{3+}$. 9: mer-$[Co(dien)_2]^{3+}$. 10: u-fac-$[Co(dien)_2]^{3+}$. 11: $\Lambda\Lambda\Lambda\Delta$-$[Co(linpen)]^{3+}$. 12: $\Lambda\Delta\Lambda$-$[Co(penten)]^{3+}$. 13: Δ-$[Co(R,R\text{-}ptn)_3]^{3+}$. 14: Λ-fac-$[Co(R,S\text{-}ptn)_3]^{3+}$. 15: Λ-$[Co(R,R\text{-}ptn)_3]^{3+}$. 16: Λ-$[Co(S,S\text{-}cptn)_3]^{3+}$. 17: Λ-$[Co(sen)]^{3+}$. 18: $(-)_{589}$-$[Co(R\text{-}2\text{-}Me\text{-}tacn)_2]^{3+}$.[7)]

In Fig. 2 are plotted the λ_{max} values of the $^1T_{1g}$ transition against the average Co-N bond lengths of $[Co(N)_6]^{3+}$ complexes which contain only amine ligands. In cases where several crystallographic data are available for one complex cation, their average value is plotted. Thus, the data point for $[Co(en)_3]^{3+}$, for example, is the average of three complexes, Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$, Λ-$[Co(en)_3]Cl_3\cdot H_2O$, and $[Co(en)_3]_2(HPO_4)_3\cdot 9H_2O$. Standard deviations in the Co-N bond lengths are indicated by horizontal bars. Within these experimental uncertainties, a broad correlation seems to hold. An open circle in Fig. 2 is for $[Co(L)(en)](ClO_4)_3$ and falls in the correlation region. Thus, the following conclusion may be drawn. Since the 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 can not be properly assessed. 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 length, which resulted, of course, from the cyclic and tetradentate nature of the L ligand.

The authors are grateful to Dr. Yoshimasa Fukazawa for many helpful suggestions.

References

1) U. Sakaguchi, A. Tsuge, and H. Yoneda, Inorg. Chem., 22, 1630(1983); U. Sakaguchi, A. Tsuge, and H. Yoneda, ibid., in press.

2) H. Okazaki, U. Sakaguchi, and H. Yoneda, Inorg. Chem., 22, 1539(1983).

3) A. Werner and R. Feenstra, Ber., 39, 1538(1906).

4) J. E. Sarneski and F. L. Urbach, J. Am. Chem. Soc., 93, 884(1971).

5) See, for example; D. J. Royer, G. J. Grant, D. G. Van Derveer, and M. J. Castillo, Inorg. Chem., 21, 1902(1982).

6) Crystallographic data are taken from the following. Acta Crystallogr., Sect.B, 25, 2562(1969); Sect.B, 26, 226, 1492(1970); Sect.B, 27, 2187(1971); Sect.B, 28, 470, 2709, 3591(1972); Sect.B, 29, 739, 2438, 2443(1973); Sect.B, 30, 2126 (1974); Sect.B, 31, 931, 1378, 2456(1975); Sect.B, 33, 860, 1485(1977); Sect. B, 34, 420(1978); Sect.B, 35, 1608, 2389(1979). J. Chem. Soc., Dalton Trans., 1976, 251. Bull. Chem. Soc. Jpn., 42, 1016(1969). Acta Chem. Scand., 26, 3413(1972). Inorg. Chem., 10, 1486(1971); 16, 231(1977); 22, 1539(1983). Absorption data are taken from the following. J. Am. Chem. Soc., 93, 884 (1971). Acta Chem. Scand., Ser.A, 28, 385(1974). Inorg. Chem., 15, 2123 (1976); 16, 231(1977). Chem. Lett., 1974, 57. Inorg. Chim. Acta, 29, 211 (1978). Bull. Chem. Soc. Jpn., 45, 2129, 3451(1972); 46, 3448(1973); 50, 898, 2325, 3216(1977).

7) Abbreviations; pn = 1,2-propanediamine, chxn = trans-1,2-cyclohexanediamine, tn = 1,3-propanediamine, tmd = 1,4-butanediamine, tame = 1,1,1-tris(2-aminoethyl)ethane, dien = 3-azapentane-1,5-diamine, linpen = 3,6,9,12-tetraazatetradecane-1,14-diamine, 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.

(Received November 24, 1983)