November, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 3473—3476 (1982) 3473

Characterization of Cobalt(III) Complexes with L-Penicillaminate. Crystal Structure of (Diethylenetriamine)(L-penicillaminato)-cobalt(III) Chloride Monohydrate

Ken-ichi Okamoto,* Katsuhiko Wakayama, Hisahiko Einaga,† Masaaki Ohmasa,† and Jinsai Hidaka

Department of Chemistry, University of Tsukuba, Ibaraki 305
†*Institute of Materials Science, University of Tsukuba, Ibaraki 305*

(Received April 7, 1982)

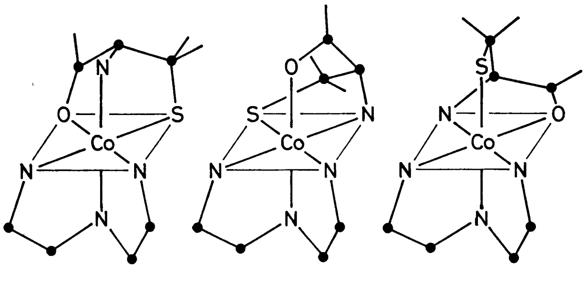
The crystal structure of the title complex, which was chromatographically obtained as the first eluted isomer, has been determined by the X-ray diffraction method. The dark-brown needle crystal was hexagonal, space group $P6_1$, $a=21.035(5)$, $c=6.459(3)$ Å, $Z=6$, and the final R value was 0.076 for 1504 non-zero reflections. Of three possible isomers for the (diethylenetriamine)(L-penicillaminato)cobalt(III) complex, the complex isolated has $\mathit{trans}(N_1N)$ configuration. The average Co–N distance for the nitrogen atoms bonded cis to the sulfur atom is 1.961 Å, whereas the trans Co–N length is 2.007 Å.

Some cobalt(III) complexes with thiolato ligands such as penicillamine and cysteine have been investigated for their stereochemical and biochemical interests.[1–3] It appears that the presence of a thiolato donor atom in the coordination sphere induces an extreme specificity concerned with the formation of possible isomers.[2,3] This work deals with the stereochemistry of the mixed cobalt(III) complex with the L-penicillaminate (L-pen) and diethylenetriamine (dien) ligands, where L-pen functions as a tripod-like terdentate ligand and has a similar framework to the L-cysteinate ion. For the $[\mathrm{Co(L\text{-}pen)(dien)}]^+$ complex having a thiolato donor atom, three geometrical isomers are possible. They are designated as $\mathit{trans}(N_1N)$, $\mathit{trans}(N_1O)$, and $\mathit{trans}(N_1S)$ with respect to the coordinated atoms as shown in Fig. 1. These isomers belong to a $\mathit{cis}(SO)$-$[\mathrm{Co(N)_4(S)(O)}]$ type and it is difficult to assign spectrochemically their geometrical configurations.

The present paper deals with the crystal and molecular structure of $[\mathrm{Co(L\text{-}pen)(dien)}]\mathrm{Cl\cdot H_2O}$ which was isolated from the first eluate by means of a column chromatographic separation. The trans effect due to the coordinated thiolato donor atom in the L-pen ligand is also discussed. A preliminary report has been presented.[4]

Experimental

(Diethylenetriamine)(L-penicillaminato)cobalt(III) chloride was prepared by a modification of a method in the literatures.[5] To a suspension containing 5.4 g of $[\mathrm{CoCl_3(dien)}]$[6] in 100 cm^3 of water was added a solution containing 5.1 g of silver nitrate in 20 cm^3 of water. The precipitated silver chloride was filtered off. After nitrogen gas was vigorously bubbled into the filtrate for 30 min, an aqueous solution containing 3.0 g of L-penicillamine was added to it. The nitrogen gas was constantly bubbled into the mixture at room temperature for about 20 h. The reaction mixture was poured onto a column (30 mm × 1000 mm) containing cation exchange resin (Dowex 50W-X8, 200—400 mesh, Na$^+$ form). After the column had been swept with water, the adsorbed band was eluted with 0.075 mol dm^{-3} aqueous solution of NaCl. Three brown bands were eluted in succession. The first eluate was concentrated to a small volume with a rotary evaporator below 15 °C. The deposited NaCl was filtered off and a large amount of ethanol–acetone (1:2) mixture added to the filtrate. The solution was kept in a refrigerator overnight. The crude crystals were collected by filtration. The dark-brown needle crystals were obtained by recrystallization from a small amount of water by adding acetone.



(a) (b) (c)

Fig. 1. Three possible isomers of $[\mathrm{Co(L\text{-}pen)(dien)}]^+$; (a) $\mathit{trans}(N_1N)$, (b) $\mathit{trans}(N_1O)$, and (c) $\mathit{trans}(N_1S)$.

Preliminary photographic examination established a hexagonal unit cell containing six chemical units of $[\mathrm{Co(L\text{-}pen)(dien)}]\mathrm{Cl\cdot H_2O}$. The systematic absence led to the space group $P6_1$. The least-squares refinement of setting angles of 41 reflections, measured on a Rigaku Denki automatic four circle diffractometer (AFC-5) using Mo $K\alpha$ radiation monochromatized by a graphite plate, led to the cell constants: $a=21.035$ (5) Å, $c=6.459$ (3) Å. The calculated density of 1.46 g cm^{-3} agrees with the observed density of 1.49 g cm^{-3} by the flotation method.

The intensity data up to $2\theta<55°$ were collected by use of ω-2θ scanning technique, the scanning rate being 4° in ω per minute. During the course of the data collection, three reflections were monitored every 100 reflections. The intensity data were converted to the F_o data in the usual manner. Absorption corrections were not applied. The standard deviations were estimated by counting statistics. A total of 1504 independent reflections with $F_o>3\sigma(F_o)$ were retained as observed, and employed in solving and refining the structure.

The electronic absorption spectra were recorded with a JASCO UVIDEC-1 spectrophotometer, and the CD spectra, with a JASCO J-20 spectropolarimeter. All measurements were carried out in aqueous solution at room temperature.

Determination of Crystal Structure

The position of the cobalt atom was obtained from the three-dimentional Patterson function. Fourier and

TABLE 1. THE ATOMIC POSITIONAL PARAMETERS, WITH THEIR e.s.d.'s IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2 a)
Co	0.4304(1)	0.1098(1)	0.1250	2.56
S	0.8796(2)	0.2085(2)	0.4666(7)	3.42
Cl	0.4363(2)	−0.0881(2)	0.0755(6)	4.03
O(1)	0.5903(5)	−0.0792(6)	0.3399(14)	3.48
O(2)	0.6732(6)	0.0167(6)	0.1524(16)	4.25
O(3)	0.6012(7)	0.7669(7)	0.2468(20)	6.66
N(1)	0.3610(6)	0.0064(6)	0.1855(17)	2.87
N(2)	0.4965(6)	0.2120(6)	0.0394(18)	3.21
N(3)	0.4534(7)	0.1441(7)	0.4117(17)	3.79
N(4)	0.5183(6)	0.0968(6)	0.0978(17)	3.25
C(1)	0.2611(8)	0.0242(8)	0.0665(25)	3.84
C(2)	0.1943(10)	0.2145(10)	0.0430(27)	5.30
C(3)	0.2109(8)	−0.0137(9)	0.2536(27)	4.79
C(4)	0.3062(7)	−0.0146(7)	0.0207(21)	3.08
C(5)	0.6514(8)	−0.0149(8)	0.3215(21)	3.54
C(6)	0.5068(11)	0.2594(9)	0.2205(25)	5.36
C(7)	0.7118(10)	0.4891(10)	0.0842(23)	5.60
C(8)	0.4343(8)	−0.2182(8)	0.4498(27)	4.08
C(9)	0.5870(7)	0.1689(8)	0.0675(24)	3.47

a) B_{eq} is the equivalent isotropic temperature factors defined by Hamilton.[17)]

difference-Fourier maps based on the cobalt atom revealed the rest of the structure. The structure was refined by a full-matrix least-squares refinement of the positional and anisotropic thermal parameters (program RFINE by L. W. Finger, which was modified by H. Horiuchi (1979), was used). The final R values in the space groups $P6_1$ and $P6_5$ converged 0.076 and 0.077, respectively, using the anomalous scattering factors. Taking the known absolute configuration of the L-penicillaminate in the complex into consideration, the space group must be $P6_1$. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[7)] The calculations were carried out on a FACOM M-200 computer at the University of Tsukuba. The final atomic parameters and their standard deviations are given in Table 1. A list of the anisotropic thermal parameters and a table of the observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8248).

Results and Discussion

Description of the Structure. A perspective drawing of the complex cations obtained is given in Fig. 2 and their packing mode is illustrated in Fig. 3. The atomic numbering scheme is given in Figs. 2 and 3. The bond lengths and angles with their estimated standard deviations in the complex ions are listed in Table 2. The coordination geometry around the cobalt atom is approximately octahedral. The L-penicillaminate and diethylenetriamine coordinate facially to the cobalt atom as terdentate ligands. The nitrogen atom of the L-pen ligand occupies the trans position to the imino nitrogen atom of the dien ligand. Therefore, this cation is determined to have a *trans(N$_i$N)* configuration as shown in Fig. 1 (a).

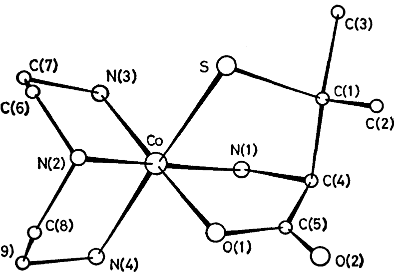


Fig. 2. A perspective drawing of *trans(N$_i$N)*-[Co(L-pen)(dien)]$^+$ with the numbering scheme of atoms.

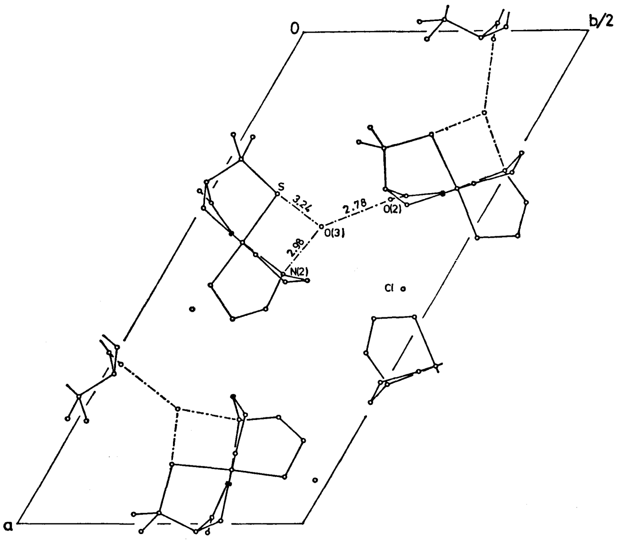


Fig. 3. A projection of the crystal packing viewed along the c axis.

The bond lengths and angles are similar to those for the cobalt(III) complexes with diethylenetriamine and/or sulfur-containing amino carboxylates.[2,8–12)] The averages of the cobalt-ligand bond lengths are 2.255 (5) Å for Co–S, 1.926 (9) Å for Co–O, and 1.972 (11) Å for Co–N. The Co–N distance involving the nitrogen atom bonded trans to the sulfur atom is 2.007 Å and the average cis Co–N distance is 1.961 Å, giving a difference between trans and cis distances of 0.046 Å. This fact suggests that the trans effect due to the coordinated sulfur atom and the difference (0.046 Å) corresponds with those of the cobalt(III) complexes with the thiolato ligands such as 2-aminoethanethiolate.[13)]

The crystal structure consists of the complex cations, chloride anions, and water molecules. As shown in Fig. 3, a water molecule O(3) atom is surrounded by the three atoms: *e.g.*, the oxygen O(2) atom of the complex cation and the sulfur S and nitrogen N(2) atoms of the other complex cation. The O(3)–O(2) or O(3)–N(2) distance is mostly less than 3 Å and O(3)–S one is 3.24 Å. These distances suggest that those are hydrogen bonds.

In order to examine the conformations of chelate rings, the displacements of relevant atoms from the chelate ring plane, which is defined by the central

TABLE 2. INTERMOLECULAR DISTANCES AND BOND ANGLES (WITH e.s.d.'s) FOR $trans(N_1N)$-[Co(L-pen)(dien)]Cl·H_2O

Bond distance	l/Å	Bond distance	l/Å
Co-S	2.255(5)	N(4)-C(9)	1.494(14)
Co-O(1)	1.926(9)	O(1)-C(5)	1.326(14)
Co-N(1)	1.959(10)	O(2)-C(5)	1.240(17)
Co-N(2)	1.967(10)	C(1)-C(2)	1.546(26)
Co-N(3)	1.957(11)	C(1)-C(3)	1.538(22)
Co-N(4)	2.007(15)	C(1)-C(4)	1.558(27)
S-C(1)	1.852(13)	C(4)-C(5)	1.509(19)
N(1)-C(4)	1.465(18)	C(6)-C(7)	1.512(26)
N(2)-C(6)	1.480(21)	C(8)-C(9)	1.523(26)
N(3)-C(7)	1.482(19)		
Bond angle	ϕ/°	Bond angle	ϕ/°
S-Co-N(1)	83.6(4)	S-N(3)-C(7)	111.0(11)
S-Co-N(2)	94.8(5)	Co-N(4)-C(9)	111.3(11)
S-Co-N(3)	90.7(5)	Co-O(1)-C(5)	111.6(8)
S-Co-N(4)	175.9(3)	S-C(1)-C(2)	111.4(12)
S-Co-O(1)	89.4(4)	S-C(1)-C(3)	109.8(11)
N(1)-Co-N(2)	174.9(5)	S-C(1)-C(4)	106.2(9)
N(1)-Co-N(3)	97.5(5)	C(2)-C(1)-C(3)	110.0(13)
N(1)-Co-N(4)	95.3(5)	C(2)-C(1)-C(4)	110.9(14)
N(1)-Co-O(1)	84.3(4)	C(3)-C(1)-C(4)	108.5(14)
N(2)-Co-N(3)	87.3(5)	N(1)-C(4)-C(1)	107.3(12)
N(2)-Co-N(4)	85.9(5)	N(1)-C(4)-C(5)	106.3(11)
N(2)-Co-O(1)	90.9(4)	C(1)-C(4)-C(5)	109.6(14)
N(3)-Co-N(4)	93.3(6)	O(1)-C(5)-O(2)	122.4(12)
N(3)-Co-O(1)	178.2(4)	O(1)-C(5)-C(4)	114.6(11)
N(4)-Co-O(1)	86.6(5)	O(2)-C(5)-C(4)	123.0(11)
Co-S-C(1)	97.9(6)	N(2)-C(6)-C(7)	110.3(16)
Co-N(1)-C(4)	103.2(8)	N(3)-C(7)-C(6)	109.0(12)
Co-N(2)-C(6)	107.5(8)	N(2)-C(8)-C(9)	110.5(12)
Co-N(2)-C(8)	109.0(10)	N(4)-C(9)-C(8)	106.9(12)

TABLE 3. DISPLACEMENTS OF ATOMS FROM THE LEAST-SQUEARES PLANE (d/Å)

Diamine chelate ring:			
Plane 1; $-0.9856X+0.1689Y+0.0085Z+7.4323=0$			
Co	0.0001	C(6)	0.4312
N(2)	0.0000	C(7)	−0.1352
N(3)	0.0000		
Plane 2; $-0.1161X-0.2647Y-0.9573Z+2.2171=0$			
Co	0.0000	C(8)	0.3621
N(2)	0.0000	C(9)	−0.2393
N(4)	0.0000		
S-N chelate ring			
$-0.0401X-0.1954Y-0.9799Z+1.4969=0$			
Co	0.0000	C(1)	0.7804
S	0.0000	C(4)	1.1540
N(1)	0.0001		
O-N chelate ring			
$-0.9810X+0.1942Y+0.0012Z+7.3511=0$			
Co	0.0000	C(4)	0.8379
O(1)	0.0000	C(5)	0.3712
N(1)	0.0000		

The X, Y, and Z coordinates in Å are referred to the crystallographic axes.

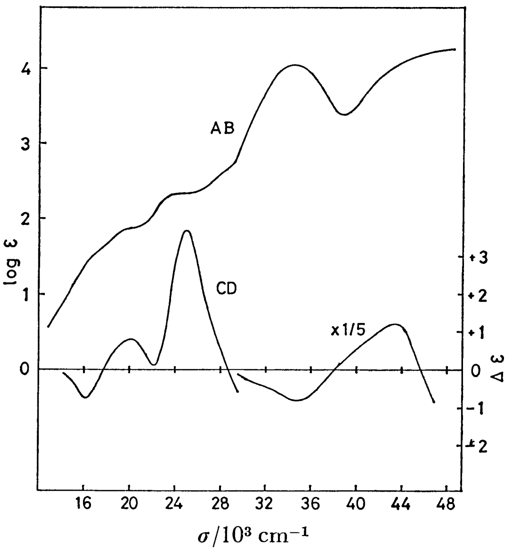


Fig. 4. Absorption and CD spectra of $trans(N_1N)$-[Co(L-pen)(dien)]$^+$.

cobalt atom and the two coordinated atoms in the chelate ring, were calculated. The results are given in Table 3. The diamine chelate rings in the dien ligand take reasonable conformations,[8] δ form for N(2)–C(8)–C(9)–N(4) and λ one for N(2)–C(6)–C(7)–N(3). The N–S chelate ring in the L-pen ligand has a similar conformation to that of the $trans(O)$-[Co(R,R-ebsmc)]$^+$ complex, where R,R-ebsmc denotes N,N'-ethylenebis(S-methyl-L-cysteinate) which has the same frame-work as the L-pen ligand.[9]

Electronic Absorption and CD Spectra. The electronic absorption and CD spectra of the $trans(N_1N)$-[Co(L-pen)(dien)]$^+$ complex are shown in Fig. 4. The sulfur-to-metal charge transfer band of this complex is observed at 34.5×10^3 cm^{-1}, as in the case of the cobalt(III) complexes with thiolato and thioether ligands.[3,9,14] In the first absorption band region, the complex shows an explicit shoulder (*ca.* 16.7×10^3 cm^{-1}) on the lower energy side of the major peak (20.0×10^3 cm^{-1}) and the lower energy component is characteristic of thiolato coordination.[3,15] The absorption spectrum of this complex shows comparatively intense humps in the region from 23×10^3 cm^{-1} to 28×10^3 cm^{-1} and an intense positive CD band ($\Delta\varepsilon$ +3.75 at 25.0×10^3 cm^{-1}) in appearance corresponds to the humps. The absorption and CD spectral behavior in this region are common to those of the $trans(N_1O)$- and $trans(N_1S)$-[Co(L-pen)(dien)]$^+$ complexes.[4,16] Similar spectral patterns are observed for the [Co(L-pen)$(NH_3)_3$]$^+$ complex, which belongs to the $cis(SO)$-[Co(N)$_4$(S)(O)] type. It does not have chirality arising from the skew pair of chelate rings because of the coordination of three ammonia molecules instead of dien.[16] Taking these facts into account, it can be considered that the absorption and CD bands in this region are characteristic of the coordinated thiolato donor atom of the ligand.

References

1) G. Gorin, J. E. Spessard, G. A. Wessler, and J. P. Oliver, *J. Am. Chem. Soc.*, **81**, 3193 (1959); W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, **17**, 2165 (1978); H. C. Freeman, C. J. Moore, W. G. Jackson, and A. M. Sargeson, *ibid.*, **17**, 3513 (1978).

2) P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, **99**, 101 (1977); H. M. Helis, P. de Meester, and D. J. Hodgson, *ibid.*, **99**, 3309 (1977).

3) K. Yamanari, N. Takeshita, T. Komorita, and Y. Shimura, *Chem. Lett.*, **1981**, 861.

4) K. Okamoto, K. Wakayama, M. Ohmasa, and J. Hidaka, *Chem. Lett.*, **1981**, 453.

5) J. L. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966); K. Okamoto, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **48**, 2425 (1975).

6) P. H. Crayton, *Inorg. Synth.*, **7**, 207 (1963).

7) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1974), Vol. IV.

8) M. Konno, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 739 (1973).

9) K. Okamoto, T. Isago, M. Ohmasa, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **55**, 1077 (1982).

10) P. de Meester and D. J. Hodgson, *J. Chem. Soc., Dalton Trans.*, **1976**, 618.

11) R. C. Elder, G. J. Kennard, M. D. Payne, and E. Deutsch, *Inorg. Chem.*, **17**, 1296 (1978).

12) R. J. Magee, W. Mazurek, M. J. O'Connor, and A. T. Phillip, *Aust. J. Chem.*, **27**, 1629 (1974).

13) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **13**, 2360 (1974); B. A. Lange, K. Libson, E. Deutsch, and R. C. Elder, *ibid.*, **15**, 2985 (1976); R. C. Elder, M. J. Heeg, M. D. Payne, M. Trkula, and E. Deutsch, *ibid.*, **17**, 431 (1978).

14) T. Isago, K. Igi, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **52**, 407 (1979); K. Yamanari, J. Hidaka, and Y. Shimura, *ibid.*, **50**, 2299 (1977).

15) V. H. Houlding, H. Mäcke, and A. W. Adamson, *Inorg. Chem.*, **20**, 4279 (1981).

16) The present authors, to be published.

17) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).