March, 1984] © 1984 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 57, 877—878 (1984)

# Preparation and Crystal Structure of Bis[(2-aminoethyl)dimethylphosphine][1,2-bis(dimethylphosphino)ethane]cobalt(III) Tribromide Dihydrate, $[Co\{NH_2CH_2CH_2P(CH_3)_2\}_2\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}]Br_3 \cdot 2H_2O$

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(Received August 25, 1983)

**Synopsis.** The title compound has been prepared and the crystal structure determined by the X-ray diffraction method. The complex ion is the *trans(P, N)* isomer, where one of the N atoms of (2-aminoethyl)dimethylphosphine (edmp) occupies the position trans to the P atom of the other edmp ligand.

In the course of our preparative studies[1,2] of the series-complexes $[Co(en)_x(edmp)_y(dmpe)_z]^{3+}(x+y+z=3)$, where en, edmp, and dmpe denote ethylenediamine, (2-aminoethyl)dimethylphosphine, and 1,2-bis(dimethylphosphino)ethane, respectively, we have obtained $[Co(edmp)_2(dmpe)]Br_3 \cdot 2H_2O$ by the reaction of *trans*-$[CoCl_2(edmp)_2]ClO_4$ with dmpe. There are three possible geometrical isomers of the complex ion (Fig. 1). In order to determine the geometrical configuration, crystals of the complex have been subjected to X-ray structure analysis.

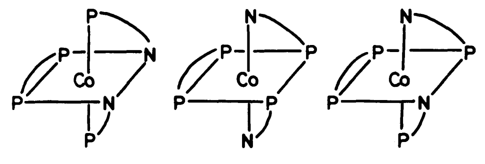
trans(P, P) trans(N, N) trans(P, N)

Fig. 1. Three geometrical isomers of $[Co(dmpe)(edmp)_2]^{3+}$.

## Experimental

*Preparation of the Complex.* To an oxygen-free methanol solution ($50\,cm^3$) of *trans*-$[CoCl_2(edmp)_2]ClO_4$[3] (205 mg, 0.467 mmol) was added dropwise an oxygen-free methanol solution ($50\,cm^3$) of dmpe[2] (70 mg, 0.467 mmol) with stirring under an atmosphere of nitrogen at room temperature. After 12 h the resulting yellow solution was filtered to remove yellow precipitate of *fac*-$[Co(edmp)_3]X_3$ ($X=Cl^-$ or $ClO_4^-$).[1] The filtrate was diluted with water ($1\,dm^3$) and poured on a column ($\phi$ 3×120 cm) of SP-Sephadex C-25. The adsorbed product was eluted with $0.2\,mol\,dm^{-3}$ NaCl, giving two main yellow bands with several minor ones. The complex of the second main band was *fac*-$[Co(edmp)_3]^{3+}$. The eluate of the first main band was evaporated to dryness under reduced pressure, and the complex was extracted with a small amount of methanol. The extract was diluted several times with water and rechromatographed in a similar manner using a small column ($\phi$ 1×10 cm) and $1\,mol\,dm^{-3}$ NaBr. The yellow eluate was concentrated to a small volume in a desiccator over $P_4O_{10}$ to yield orange yellow crystals. Yield: 13 mg (4%). Most of the reaction product was *fac*-$[Co(edmp)_3]^{3+}$. Found: C, 24.32; H, 6.11, N, 4.07%. Calcd for $C_{14}H_{44}N_2Br_3CoOP_2=[Co(edmp)_2(dmpe)]Br_3 \cdot 2H_2O$: C, 24.19; H, 6.38; N, 4.03%. The complex is soluble in water and alcohols, but insoluble in nonpolar solvents such as chloroform.

*Crystal Structure Determination.* Crystals are prismatic b. Crystal data are; monoclinic, $P2_1/a$, $a=16.380(5)$, $b=19.845(6)$, $c=9.538(3)$ Å, $\beta=122.34(2)°$, $V=2619.4(14)$ Å$^3$, $Z=4$, $D_x=1.76$, $D_m=1.76(2)\,Mg\,m^{-3}$, MW=695.1, $\lambda(Mo\,K\alpha)=0.70926$ Å, $\mu=5.44\,mm^{-1}$. The intensity measurements were performed to $2\theta=60°$ ($+h$, $-k$, $\pm l$ set) on a Rigaku AFC-5 four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate and with a crystal of $0.2\times0.2\times0.2\,mm^3$ in dimensions. 6613 reflections were measured and 3299 unique ones were obtained. Lorentz, polarization and absorption corrections were applied.[4] The structure was solved by direct methods with MULTAN78.[5] Starting with the positions of the Co and three Br atoms those of the other non-H atoms were determined from electron-density maps and refined by block-diagonal least squares with anisotropic thermal parameters using UNICS III computation program system.[6] The psitions of all the H atoms were calculated except those of water molecules and not refined. Final $R$ was 0.071, $wR=0.071$, $S=2.2$ for 3299 unique reflections. Complex neutral-atom scattering factors were taken from International Tables for X-Ray Crystallography.[7]

## Results and Discussion

Final atomic parameters of non-H atoms are presented in Table 1 and a perspective drawing of the complex cation in Fig. 2.[8] This is the *trans(P, N)* isomer. Bond lengths and bond angles are listed in Table 2.

Table 1. Fractional coordinates and isotropic temperature factors

| Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| Co | 0.2848(1) | 0.12353(6) | 0.5100(2) | 1.2 |
| Br(1) | 0.4545(1) | 0.12588(7) | 0.2550(2) | 3.3 |
| Br(2) | 0.2767(1) | 0.36314(7) | 0.0084(2) | 3.6 |
| Br(3) | 0.4928(1) | 0.38548(6) | 0.7407(2) | 2.9 |
| P(1) | 0.1218(2) | 0.1358(1) | 0.3250(3) | 1.7 |
| P(2) | 0.2646(2) | 0.0326(1) | 0.6282(4) | 1.7 |
| P(3) | 0.2833(2) | 0.1996(1) | 0.6868(3) | 1.6 |
| P(4) | 0.4490(2) | 0.1314(1) | 0.6904(3) | 1.6 |
| N(1) | 0.2951(6) | 0.1915(4) | 0.3588(10) | 1.7 |
| N(2) | 0.2996(6) | 0.0544(4) | 0.3642(10) | 1.8 |
| C(1) | 0.1195(7) | 0.2023(5) | 0.1905(13) | 2.0 |
| C(2) | 0.2084(9) | 0.1964(6) | 0.1848(13) | 2.8 |
| C(3) | 0.2657(10) | -0.0354(6) | 0.5002(17) | 3.4 |
| C(4) | 0.3180(11) | -0.0163(6) | 0.4210(16) | 3.8 |
| C(5) | 0.4078(8) | 0.2200(6) | 0.8549(13) | 2.5 |
| C(6) | 0.4742(8) | 0.1593(6) | 0.8919(13) | 2.2 |
| C(7) | 0.0367(8) | 0.1622(6) | 0.3793(15) | 2.9 |
| C(8) | 0.0555(8) | 0.0675(6) | 0.1827(13) | 2.7 |
| C(9) | 0.1525(8) | 0.0187(6) | 0.6167(13) | 2.3 |
| C(10) | 0.3524(9) | 0.0062(6) | 0.8391(15) | 3.5 |
| C(11) | 0.2344(8) | 0.2820(5) | 0.6042(14) | 2.4 |
| C(12) | 0.2267(8) | 0.1778(6) | 0.7990(14) | 2.2 |
| C(13) | 0.5075(8) | 0.1983(6) | 0.6446(13) | 2.6 |
| C(14) | 0.5279(8) | 0.0601(6) | 0.7265(14) | 2.6 |
| O(1) | 0.3168(6) | 0.3355(4) | 0.3766(10) | 3.4 |
| O(2) | 0.1867(7) | 0.0267(5) | 0.0090(10) | 4.3 |

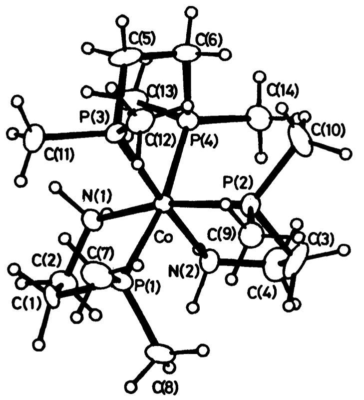

Fig. 2. An ORTEP drawing of the complex cation with thermal ellipsoids scaled at the 50% probability level.[9] H atoms are represented by circles of radius 0.08 Å.

Table 2. Bond lengths ($l$/Å) and angles ($\phi$/°) and their estimated standard deviations

| | | | |
|---|---|---|---|
| Co -P(1) | 2.294( 3) | P(3) -C(5) | 1.843(10) |
| Co -P(2) | 2.245( 4) | P(3) -C(11) | 1.806(10) |
| Co -P(3) | 2.273( 4) | P(3) -C(12) | 1.803(17) |
| Co -P(4) | 2.295( 3) | P(4) -C(6) | 1.823(13) |
| Co -N(1) | 2.047(10) | P(4) -C(13) | 1.822(14) |
| Co -N(2) | 2.058(10) | P(4) -C(14) | 1.820(13) |
| P(1) -C(1) | 1.827(12) | N(1) -C(2) | 1.503(11) |
| P(1) -C(7) | 1.804(17) | N(2) -C(4) | 1.476(14) |
| P(1) -C(8) | 1.811(11) | C(1) -C(2) | 1.49 ( 2) |
| P(2) -C(3) | 1.827(16) | C(3) -C(4) | 1.46 ( 3) |
| P(2) -C(9) | 1.801(15) | C(5) -C(6) | 1.53 ( 2) |
| P(2) -C(10) | 1.815(11) | | |

| | | | |
|---|---|---|---|
| P(1) -Co -P(2) | 92.7( 1) | C(3) -P(2) -C(9) | 102.7( 7) |
| P(1) -Co -P(3) | 91.7( 1) | C(3) -P(2) -C(10) | 104.0( 6) |
| P(1) -Co -P(4) | 169.9( 1) | C(9) -P(2) -C(10) | 101.6( 6) |
| P(1) -Co -N(1) | 83.6( 3) | Co -P(3) -C(5) | 110.2( 3) |
| P(1) -Co -N(2) | 93.5( 3) | Co -P(3) -C(11) | 117.1( 3) |
| P(2) -Co -P(3) | 95.6( 1) | Co -P(3) -C(12) | 119.6( 5) |
| P(2) -Co -P(4) | 96.1( 1) | C(5) -P(3) -C(11) | 101.9( 4) |
| P(2) -Co -N(1) | 166.9( 3) | C(5) -P(3) -C(12) | 102.6( 6) |
| P(2) -Co -N(2) | 84.6( 3) | C(11)-P(3) -C(12) | 103.2( 6) |
| P(3) -Co -P(4) | 82.7( 1) | Co -P(4) -C(6) | 108.9( 4) |
| P(3) -Co -N(1) | 97.1( 3) | Co -P(4) -C(13) | 115.2( 5) |
| P(3) -Co -N(2) | 174.8( 3) | Co -P(4) -C(14) | 121.2( 4) |
| P(4) -Co -N(1) | 88.7( 3) | C(6) -P(4) -C(13) | 100.3( 6) |
| P(4) -Co -N(2) | 92.1( 3) | C(6) -P(4) -C(14) | 107.4( 6) |
| N(1) -Co -N(2) | 83.1( 4) | C(13)-P(4) -C(14) | 101.6( 6) |
| Co -P(1) -C(1) | 101.2( 4) | Co -N(1) -C(2) | 115.8( 6) |
| Co -P(1) -C(7) | 124.7( 5) | Co -N(2) -C(4) | 117.4( 8) |
| Co -P(1) -C(8) | 118.8( 4) | P(1) -C(1) -C(2) | 108.4( 8) |
| C(1) -P(1) -C(7) | 105.2( 6) | N(1) -C(2) -C(1) | 109.2(11) |
| C(1) -P(1) -C(8) | 103.6( 5) | P(2) -C(3) -C(4) | 111.8(11) |
| C(7) -P(1) -C(8) | 100.8( 6) | N(2) -C(4) -C(3) | 112.0(14) |
| Co -P(2) -C(3) | 101.6( 5) | P(3) -C(5) -C(6) | 110.3( 8) |
| Co -P(2) -C(9) | 120.8( 5) | P(4) -C(6) -C(5) | 105.3( 7) |
| Co -P(2) -C(10) | 123.1( 4) | | |

Bond length of Co–P(1) is longer than Co–P(2) by 0.049(4) Å, indicating trans influence of the ligating P atoms. A difference of 0.022(4) Å is also found in the bond distances between Co and P atoms of the dmpe ligand, which may be less meaningful since two Co–P bond lengths in $[Co(en)_2(dmpe)]^{3+}$ differ by 0.016(3) Å.[10] The five-membered chelate ring formed by the dmpe ligand takes an envelope conformation as shown in Fig. 3. Conformation of the same ligand in $[Co(en)_2(dmpe)]^{3+}$ is a twisted (gauche) one. The asymmetry of the ring conformation may be caused to release the steric repulsion between two methyl groups, C(9) and C(12) [3.49(2) Å]. The methyl C(13) atom is in close contact with the N(1) atom [3.07(1) Å].

In the *trans(P, P)* isomer, in which the positions of P(1) and N(1) atoms are interchanged, the steric interactions between methyl groups C(9) and C(12) and between C(13) and C(7′) will render the complex unstable. The *trans(N, N)* isomer will also be unstable since it has two pairs of mutually trans P donating atoms as exemplified by the elongation of the Co–P(1) bond. This the *trans(P, N)* isomer will be the most stable among the isomers from both steric and electronic factors.

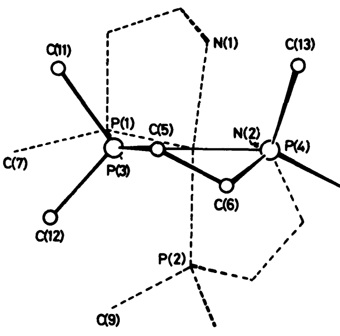

Fig. 3. The dmpe ligand viewed along the line through the Co atom and the midpoint of P(3)–P(4) axis.

The complex in aqueous solution shows an absorption spectrum very similar to that of $[Co(en)(dmpe)_2]^{3+}$,[2] giving the d-d bands at 24150 cm$^{-1}$ (log $\varepsilon$=2.79) and *ca.* 29000 cm$^{-1}$(log $\varepsilon$=2.7, shoulder), and the Co–P charge transfer band at 36900 cm$^{-1}$(log $\varepsilon$=4.42). The thermal stability is also similar to that of $[Co(en)(dmpe)_2]^{3+}$; the complex in water or other solvents is stable at room temperature, but decomposes slowly on heating. The complex in water in the presence of excess NaCl changes to *trans*-$[CoCl_2(edmp\ or\ dmpe)_2]^+$ and a small amount of Co(II) species by heating at 60—70 °C for several hours.

This work was supported by the research grant of the Takeda Science Foundation.

## References

1) I. Kinoshita, K. Kashiwabara, J. Fujita, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **54**, 2683 (1981).

2) T. Ohishi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 3441 (1983).

3) I. Kinoshita, Y. Yokota, K. Matsumoto, S. Ooi, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 1067 (1983).

4) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

5) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson (1978). MULTAN78, "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univs of York, England, and Louvain, Belgium.

6) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

7) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 71 and 148.

8) Tables of the anisotropic thermal parameters of the non-H atoms, the coordinates of H atoms and observed and calculated structure factors, and a detail of the crystal structure determination are kept as Document No. 8407 at the Chemical Society of Japan.

9) C. K. Johnson (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

10) S. Ohba, Y. Saito, T. Ohishi, K. Kashiwabara, and J. Fujita, *Acta Crystallogr., Sect. C*, **39**, 49 (1983).