BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(6), 1947—1948 (1975)

Synthesis of *trans*-Dibromo-bis{(2-pyridyl)methylamine} and -bis{*S*-1-(2-pyridyl)ethylamine}cobalt(III) Complexes

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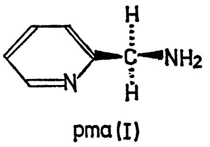
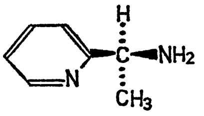
(Received January 8, 1975)

Synopsis. Light green crystals of *trans*-dibromo-bis-{(2-pyridyl)-methylamine} and -bis{*S*-1-(2-pyridyl)-ethylamine}cobalt(III) bromide have been prepared. The latter complex shows a circular dichroism (CD) spectrum enantiomeric with that of the corresponding *S*-propylenediamine complex in the first absorption band region.

Several cobalt (III) complexes with (2-pyridyl)-methylamine (pma)[1,2,3] (I) and optically active 1-(2-pyridyl)ethylamine (pea)[4] (II) have been prepared. However, these complexes are limited to tris- and *cis*-bis-diamine types, and no *trans*-bis type complex has been reported. Michelsen[3] claimed that the *trans* type complexes were not formed in the preparation of bis type complexes. In the course of our preparative work on cobalt (III) complexes with the same ligands, we have obtained *trans*-dibromo-bis(pma) and -bis(pea) cobalt (III) complexes for the first time. This paper reports the preparation of these complexes as well as circular dichroism spectrum of the pea complex.



pma (I)



pea (II)

Experimental

Ligands: (2-Pyridyl)methylamine (pma) was purchased from Aldrich Chemical Co., and used without further purification. 1-(2-Pyridyl)ethylamine (pea) was prepared according to the method described in the literature[5] and resolved with $(-)_D$-tartaric acid by a method similar to that given by Michelsen.[4] $(-)_D$-Isomer of pea is known to have *S*-configuration.[6,7] *trans*-Dibromo-bis{*S*-1-(2-pyridyl)ethylamine}-cobalt(III) hydrogen dibromide, *trans*-$[CoBr_2(S\text{-pea})_2]Br \cdot HBr$: A mixture of $NH_4[Co(SO_3)_2(NH_3)_4]$[8] (3.0 g, 0.01 mol) and *S*-pea (2.44 g, 0.02 mol) in 20 ml of water was heated at 60 °C for 2 hr with stirring. The brownish yellow solution was evaporated to dryness under reduced pressure at 60 °C and the residue dissolved in 20 ml of 48% hydrobromic acid. The solution was warmed at 60 °C for 2 hr to give light green crystals, which were filtered off, washed with a small amount of ethanol and then with ether. Found: C, 26.95; H, 3.39; N, 8.98%. Calcd for $C_{14}H_{20}N_4CoBr_4$: C, 26.50; H, 3.78; N, 9.13%. *trans*-Dibromo-bis{(2-pyridyl)-methylamine}cobalt(III) bromide monohydrate, *trans*-$[CoBr_2(pma)_2]Br \cdot H_2O$: This complex was prepared by a similar method by use of pma instead of *S*-pea. Found: C, 27.39; H, 3.18; N, 10.54%. Calcd for $C_{12}H_{18}N_4OCoBr_3$: C, 27.07; H, 3.40; N, 10.51%.

Absorption and CD spectra were recorded with a Shimadzu Double 40-R spectrophotometer and a Jasco J-20 spectropolarimeter, respectively, at room temperature.

Results and Discussion

The two dibromo complexes have light green color, characteristic of *trans*-dibromo-diamine complexes. Figure 1 shows that their absorption spectra are very similar to that of the corresponding *S*-propylenediamine (*S*-pn) complex. The present *trans*-dibromo complexes with two unsymmetrical bidentate ligands have further geometrical isomers, *cis* and *trans* with respect to the configuration of the pyridyl groups (py). However, the *cis* isomer involves a big steric hindrance between the hydrogen atoms of the two pyridyl groups and the present complex can be assigned to *trans*(Br-Br)*trans*(py-py) configuration. This assignment may be supported by the *trans*(py-py) configuration of $[Cu(S\text{-pea})_2]Cl_2 \cdot 2H_2O$.[7]

Isolation of the corresponding dichloro complexes was not successful because of their high solubility.

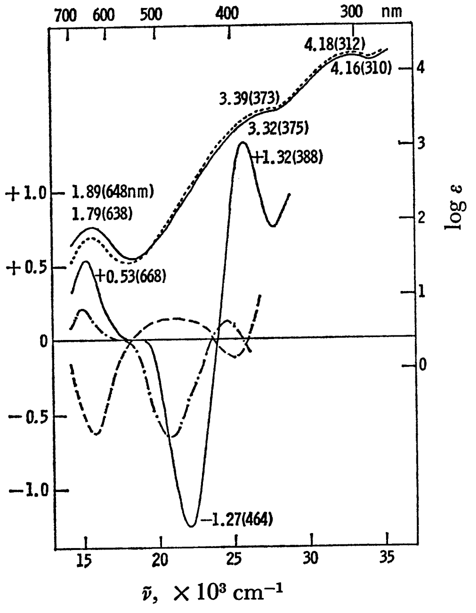


Fig. 1. Absorption spectra of (······) *trans*-$[CoBr_2(pma)_2]^+$ and (——) *trans*-$[CoBr_2(S\text{-pea})_2]^+$ in methanol. CD spectra of (——) *trans*-$[CoBr_2(S\text{-pea})_2]^+$ (----) *trans*-$[CoBr_2(S\text{-pn})_2]^+$[9] and (—·—) *trans*-$[CoCl_2(N\text{-Me}(R)\text{-en})_2]^+$[11] in methanol.

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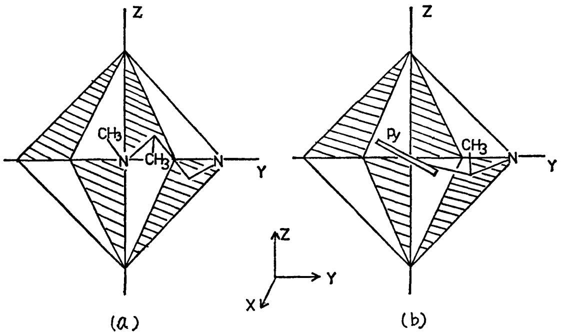

(a) (b)

Fig. 2. The hexadecadal regional rule proposed by Mason.[13]

The CD spectrum of *trans*-[$CoBr_2$(*S*-pea)$_2$]$^+$ gives a positive and a negative CD band in the region of the Ia($A_{1g}\rightarrow E_g$) and Ib ($A_{1g}\rightarrow A_{2g}$) absorption component (D_{4h} approximation), respectively (Fig. 1). This spectrum is virtually enantiomeric with that of *trans*-[CoX_2 (*S*-pn)$_2$]$^+$ ($X=Cl^-$, Br^-),[9] but very similar to those of *trans*(Cl,Cl) *trans*(*N*-CH_3, *N*-CH_3)-[$CoCl_2$ (*N*-CH_3(*R*)-*S*-pn)$_2$]$^{+}$[10] (*N*-CH_3(*R*)-*S*-pn=*N*-methyl(*R*)-*S*-propylenediamine) and -[$CoCl_2$ (*N*-CH_3(*R*)-en)$_2$]$^{+}$[11] (*N*-CH_3(*R*)-en=*N*-methyl(*R*)-ethylenediamine). X-Ray diffraction method[12] showed that three complexes have a similar conformational structure to one another.

Mason[13] proposed a hexadecadal regional rule (Fig. 2(a)) to account for the CD sign of a *trans*-dihalogeno-diamine complex. The *N*-methyl group in an unhatched region gives contribution to a negative CD for the $A_{1g}\rightarrow A_{2g}(D_{4h})$ component, while the *S*-pn has no such *N*-methyl group and its chain alkyl group lies in a hatched region where contribution to the sign is reversed. The CD sign of the $A_{1g}\rightarrow E_g(D_{4h})$ component is usually opposite to that of the $A_{1g}\rightarrow A_{2g}(D_{4h})$ owing to the partial sum-rule.[12] Detailed structure of the present dibromo complex is unknown. However, the *S*-pea chelates in [Cu(*S*-pea)$_2$]$Cl_2\cdot H_2O$[7] have slightly puckered structures and the chelates and the pyridyl rings are not co-planar. On the analogy of this X-ray analysis, the *S*-pea chelate ring in the bromo complex is depicted in Fig. 2(b). Such a twisted structure can be expected whenever the methyl group tends to take an equatorial orientation to the chelate ring. Hence most atoms in the pyridyl group seem to occupy the unhatched region and will give a CD with negative sign for the $A_{1g}\rightarrow A_{2g}(D_{4h})$ component. The *N*-methyl-*S*-pn(en) complex has asymmetric nitrogen atom but the *S*-pea complex does not. The similarity in the CD spectra between the *S*-pea and the *N*-methyl(*R*)-*S*-pn(en) complexes will thus be understood by the hexadecadal rule.

The *trans*-[$CoBr_2$(*S*-pea)$_2$]$^+$ react readily with *S*-pea in DMSO at room temperature to give [Co(*S*-pea)$_3$]$^{3+}$ consisting of all possible four diastereomers. Of these, *fac-Δ*, *fac-Λ* and *mer-Λ* were separated and isolated by SP-Sephadex column chromatography, but *mer-Δ* isomer was too little to be isolated. Michelsen[4] obtained also the first three isomers from [$CoCl_2$ py_4]$Cl\cdot 6H_2O$ and *S*-pea in pyridine using a similar column chromatography. The origin of such a stereoselective complex formation remains unknown.

References

1) G. J. Sutton, *Aust. J. Chem.*, **13**, 74, 222, 473 (1960).

2) K. Michelsen, *Acta Chem. Scand.*, **24**, 2003 (1970).

3) K. Michelsen, *ibid.*, **26**, 769 (1972).

4) K. Michelsen, *ibid.*, *A*, **28**, 428 (1974).

5) F. B. Laforge, *J. Amer. Chem. Soc.*, **50**, 2477 (1928).

6) H. E. Smith, L. J. Schaad, R. B. Banks, C. J. Wiant, and C. F. Jordan, *ibid.*, **95**, 811 (1973); O. Cervinka, O. Belovsky, and P. Rejmanova, *Z. Chem.*, **10**, 69 (1970); *Chem. Abstr.*, **72**, 110653j (1970).

7) K. Matsumoto and H. Kuroya, Private communication.

8) A. Werner and H. Gruger, *Z. Anorg. Chem.*, **16**, 398 (1898).

9) H. Ito, J. Fujita, and K. Saito, This Bulletin, **42**, 1286 (1969).

10) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Nucl. Chem. Lett.*, **5**, 203 (1969); *Inorg. Chem.*, **9**, 1476 (1970).

11) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **7**, 915 (1968); M. Kojima and T. Ishii, *Inorg. Nucl. Chem. Lett.*, **10**, 1095 (1974).

12) Y. Saito and H. Iwasaki, This Bulletin, **35**, 1131 (1962); W. T. Robinson, D. A. Buckingham, G. Chandler, L. G. Marzilli, and A. M. Sargeson, *Chem. Commun.*, **1970**, 539.

13) S. F. Mason, *J. Chem. Soc.*, *A*, **1971**, 667.