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MIXED-LIGAND COMPLEX OF COBALT(III) CONTAINING N,N'-BIS(2-PYRIDYLMETHYL)ETHYLENEDIAMINE AND ETHYLENEDIAMINE

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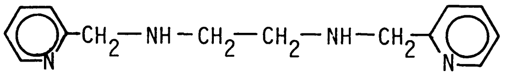
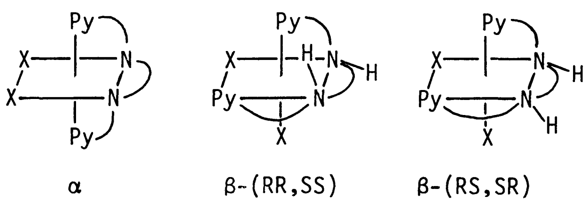
The title complex was prepared and all the geometrical isomers and the diastreoisomers were separated. The structure of each isomer was assigned in terms of ^{13}C-NMR and CD spectra.

N,N'-Bis(2-pyridylmethyl)ethylenediamine ("penp") is a linear quadridentate ligand analogous to a well-known ligand of triethylenediamine ("trien"). Cobalt(III) complexes of penp were reported by Gibson et al.[1)] and Michelsen[2)]. Any trans-isomer has not been reported yet, probably because of its sterically hindered structure. Three isomers are possible for the complex of the type: $[Co(XX)(penp)]^{n+}$ (XX = two unidentate ligand in cis position or a bidentate ligand), as Fig. 1 shows. Two β-isomers are diastereoisomers. The nomenclature in the figure is based upon the corresponding structure of the trien complex[3)]. Only two isomers have been known in the case of $X = Cl^-$ [1,2)].

The authors succeeded to prepare all the three isomers using ethylenediamine ("en") as a ligand, which occupied remaining coordination sites. The complex was prepared in the presence of active charcoal by stirring the mixture of en, en•2HCl, and $[Co(OH)(H_2O)(penp)](ClO_4)_2 \cdot 2H_2O$, mole ratio of which was 1:4:2. The isomers were separated on a column of SP-sephadex C-25, using 0.25 M Na_2SO_4



penp



α β-(RR,SS) β-(RS,SR)

$[Co(XX)(penp)]^{n+}$

Fig. 1 Three isomers of penp complex.

acidified with H_2SO_4 (pH = 2.5) as an eluent. In this communication, three isomers are called in terms of their elution order as SH1-, SH2-, and SH3-en•penp. The SH2- and SH3-isomer could not be separated when neutral Na_2SO_4 or $Na_3HP_2O_7$ (pH = 6.8) was used as an eluent.

Table 1 The Analytical and Some Other Data of the Isomers

Complex perchlorate		Co(%)	H(%)	C(%)	N(%)	R*	ν_{max}, cm^{-1} (ε)
SH1-en•penp•H_2O	Found	8.75	4.08	28.13	12.24	1.00	21,600 (105)
	Calcd	8.70	4.16	28.36	12.40		29,700 (114)
SH2-en•penp•H_2O	Found	8.70	3.99	27.87	12.36	0.32	21,300 (177)
	Calcd	8.70	4.16	28.36	12.40		29,400 (139)
SH3-en•penp	Found	8.91	4.07	30.52	13.48	0.47	21,400 (172)
	Calcd	8.93	3.97	29.13	12.74		29,700 (160)

*Molar ratio of the yield to the yield of the SH1-isomer.

The solid complex was obtained as its perchlorate. Table 1 lists the elemental analyses, molar ratio of the yield, and wavenumbers and molar absorption coefficients of the d-d bands.

Of the three isomers, SH1-en•penp is assumed to be the α-isomer, because its molar absorption coefficients are significantly less than those of the others. This assumption is supported by the ^{13}C-NMR spectrum, which was recorded on a JNM FX-60 Fourier transform spectrometer, operating at 15.1 MHz. The two-fold axis, being present in the α-isomer, reduces the resonances to halves of all the carbon atoms.

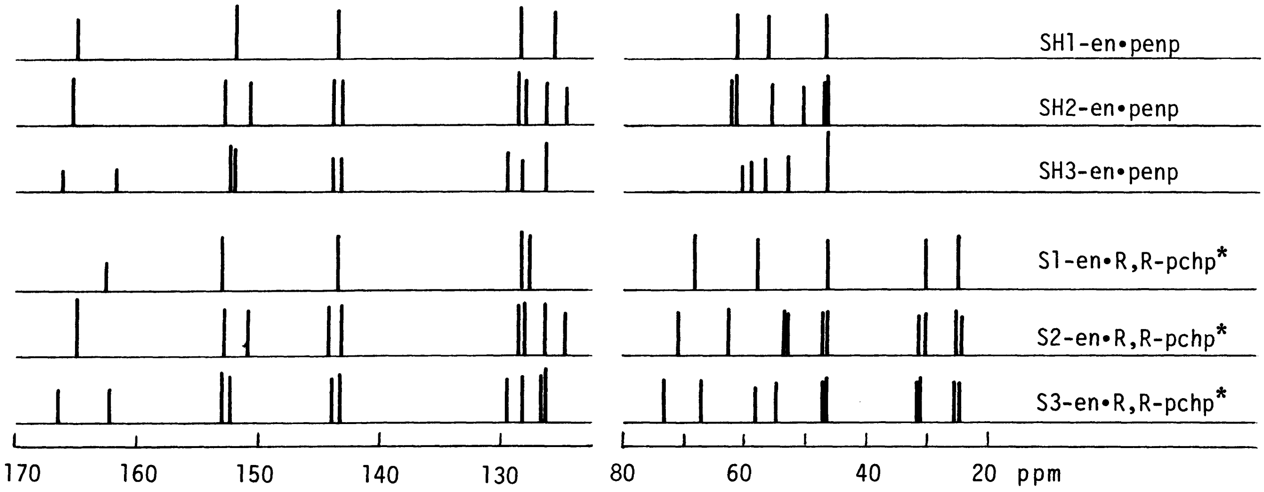


Fig. 2 Diagrammatic representation of the ^{13}C-NMR spectra in 0.05 M HCl with TMS as an external standard. *R,R-pchp is described in next page.

Two β-isomers may be characterized by their CD spectra. Fractional crystallization of β-[Co(en)(penp)][Co(cysu)$_3$]•nH$_2$O (cysu = L-cysteinesulphonate ion[4]; n is not determined), followed by separation of the isomers using a sephadex column with acidic Na$_2$SO$_4$ as an eluent, afforded each resolved isomer. Fig. 3 shows their CD spectra, which indicate that these isomers have Δ-configuration. The difference-curve is comparable with that of the reported complex, Δ-β-(RS)- and Δ-β-(RR)-[Co(gly)(trien)]I$_2$•H$_2$O[3]. Although the chromophore of both complexes is different, the resemblance of each difference-curve of both series of isomers is pronounced. Thus, SH2-en•penp and SH3-en•penp are tentatively assigned to the β-(RS,SR)- and β-(RR,SS)-isomer, respectively.

In order to ascertain their structures, N,N'-bis(2-pyridylmethyl)-1R,2R-cyclohexancediamine ("R,R-pchp") was prepared. When the ligand coordinates to a metal ion, central chelate ring is expected to be fixed to λ-conformation. Therefore, stereospecific formation of a Δ-β-(RS)-isomer and a Λ-β-(SS)-isomer is expected for the β-type isomers of [Co(en)(R,R-pchp)]$^{3+}$. Actually, column chromatographic separation of the prepared complex with neutral Na$_2$SO$_4$ as an eluent yielded S1-, S2- and S3-en•R,R-pchp, which were found to be α-, β- and β-isomer, respectively, from

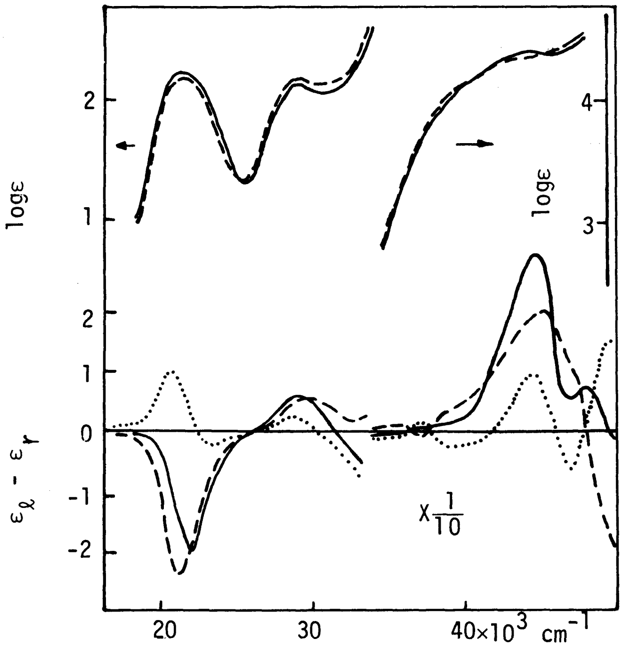


Fig. 3 AB and CD spectra of SH2-[Co(en)-(penp)]$^{3+}$ (——) and SH3-[Co(en)-(penp)]$^{3+}$ (----). Difference-curve (SH2 minus SH3) of both isomers (•••••).

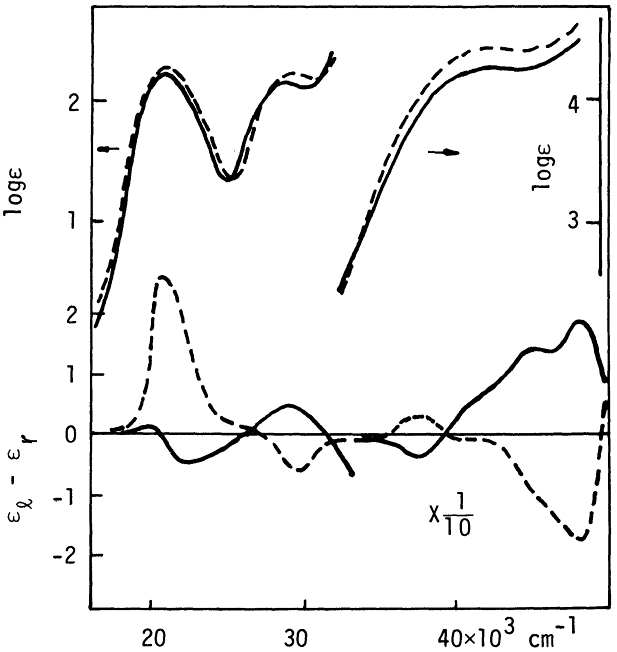


Fig. 4 AB and CD spectra of S2-[Co(en)(R,R-pchp)]$^{3+}$ (——) and and S3-[Co(en)(R,R-pchp)]$^{3+}$ (----).

their ^{13}C-NMR spectra, which are shown in Fig. 2. The spectra also indicate that S2- and S3-en•R,R-pchp are conformationally equivalent to the SH2- and SH3-en•penp, respectively. On the other hand, the configuration of S3-en•R,R-pchp can be assigned as Λ by the CD spectrum shown in Fig. 4. The S2-isomer exhibits relatively weak spectrum in the region of the first absorption band, but its ultraviolet spectrum clearly indicate that it should have an opposite configuration to the S3-isomer, i. e., Δ-configuration. This means that the S2-isomer possesses β-(RS)-conformation and the S3-isomer possesses β-(SS)-conformation. This conclusion agrees well with the tentative assignment of the structure of SH2- and SH3-en•penp described above.

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