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Circular Dichroism of *trans*-Dichlorocobalt(III) Complexes with Chiral 1,2-Diamines

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The circular dichroism (CD) spectra of *trans*-dichlorobis(diamine)cobalt(III) complexes were measured in methanol solution in the 700—200 nm region, where the diamines have the general formula of $NH_2CH(R)CH_2NH_2$ (R=isopropyl, isobutyl, *sec*-butyl, benzyl and phenyl) and belong to the *S* configuration except the phenyl-substituted one. The spectra are essentially the same as the spectrum of the (*S*)-propylenediamine ((*S*)-pn; R=methyl) complex, except for the (*R*)-*C*-phenylethylenediamine ((*R*)-phenen) complex. The variation of the *C*-substituted alkyl groups has hardly any influence on the CD of the *trans*-$[CoCl_2(diamine)_2]^+$ type complexes, demonstrating that the vicinal contribution from the *C*-substituents can be disregarded in these compounds. The *trans*-$[CoCl_2((R)\text{-phenen})_2]^+$ ion shows a CD pattern differing significantly from that of the *trans*-$[CoCl_2((R)\text{-pn})_2]^+$ ion in the first absorption band region, suggesting the significance of the vicinal effect due to the *C*-substituted phenyl group. The CD curve of *trans*-$[CoCl_2((-)_D\text{-stien})_2]^+$ ion (stien=stilbenediamine) was found to be antimeric to that of the (*R*)-phenen complex. Taking into account the anomalous vicinal effect of the phenyl groups, the absolute configuration of the $(-)_D$-stien was assigned to the (*S*,*S*) configuration.

Stereochemical features which can contribute to the circular dichroism (CD) of a dissymmetric metal complex have been classified as follows: (1) a distribution of chelate rings about the metal ion (configurational effect), (2) the puckered dissymmetric conformation of individual chelate rings (conformational effect) and (3) the presence of asymmetric groups on the ligands (vicinal effect).[1,2] Some papers indicate that ligand field CD spectra of Co(III) complexes can be differentiated between the configurational and the other two effects in such systems as tris(diamine)Co(III) ion,[3] (*S*)-aminoacidatobis(ethylenediamine)Co(III) ion[4] and tris(aminoacidato)Co(III) complexes.[5] However, it has been pointed out that differentiation between the conformational and vicinal effect is rather difficult, though the latter effect is considered to have minor contributions with respect to the 1,2-diamine chelate rings.[1—2] This may be due to the fact that restriction of the conformation is usually caused by the substitution at the C atom(s) of diamine chelates such as (*R*)-propylenediamine, 2(*R*),3(*R*)-butanediamine and 1(*R*),2(*R*)-cyclohexanediamine.

Bosnich and Harrowfield reported that the CD spectra of *trans*-$[CoCl_2((R)\text{-pn})_2]^+$ ion ((*R*)-pn=(*R*)-propylenediamine) and *trans*-$[CoCl_2((R)\text{-bn})_2]^+$ ion ((*R*)-bn=2(*R*),3(*R*)-butanediamine) are nearly the same, and the contribution of vicinal effect to optical activity is small.[2] This implies that the introduction of an alkyl group larger than the methyl group into a diamine chelate ring would result in minor changes in the shape and magnitude of CD. In order to confirm the assumption, we have prepared chiral 1,2-diamines with the general formula, $NH_2CH(R)CH_2NH_2$ (*R*=isopyl, isobutyl, *sec*-butyl and benzyl),[6] from the corresponding (*S*)-amino acids, *i.e.*, (*S*)-valine, (*S*)-leucine, (*S*)-isoleucine and (*S*)-phenylalanine, respectively, and obtained *trans*-dichlorocobalt(III) complexes with these diamines. We have also prepared (*R*)-*C*-phenylethylenediamine ((*R*)-phenen)[6] from the corresponding amino acid, (*R*)-*C*-phenylglycine, the absolute configuration of which has been established.[7] The CD spectra of the (*R*)-phenen complex and of the closely related $(-)_D$-stien (stien=stilbenediamine) complex will also be discussed in this report.

Experimental

Preparation of 1,2-Diamines. (*S*)-Valine, (*S*)-leucine and (*S*)-phenylalanine were converted into the amides according to the procedure described by Yang and Rising.[8] (*S*)-Isoleucine amide hydrochloride was obtained by the method of Smith *et al.*[9] (*R*)-phenylglycine amide was also prepared by the known method.[10] All the amino acid amides and their hydrochloride were treated with $LiAlH_4$ in dry tetrahydrofuran according to the procedure of Schnell and Karrer[11] with slight modifications as follows.

To a suspension of $LiAlH_4$ (11.4 g, 0.3 mol) in dry tetrahydrofuran (250 ml) was added 0.1 mol of amino acid amide in small portions. The mixture was stirred and heated under reflux for 24 hr, and then cooled to room temperature. Water (22 ml) was added dropwise with vigorous stirring, and the resulting slurry was stirred for further 1 hr at room temperature. The slurry was filtered by suction; the residue was extracted with tetrahydrofuran (100 ml) under reflux for 1 hr, and filtered again. The extraction was repeated once more, and the filtrate and extracts of tetrahydrofuran were combined. Excess concentrated hydrochloric acid was added, and the mixture was evaporated under reduced pressure almost to dryness. The residue was dissolved in a small volume of water, and then a concentrated sodium hydroxide solution was added in order to make the solution strongly alkaline. The separated amine layer was extracted with ether (total 300 ml). The ether extracts were dried over potassium hydroxide pellets overnight, and ether was removed by distillation under atmospheric pressure. The remaining oily liquid was distilled over potassium hydroxide pellets under atmospheric or reduced pressure. The crude diamines thus obtained were used for preparing cobalt (III) complexes without further purification.

$(-)_D$-Stilbenediamine was prepared and resolved by the known method.[12]

Preparation of Complexes. The *trans*-$[CoCl_2(diamine)_2]ClO_4$ type complexes of (*S*)-ipren, (*S*)-*i*-buen and (*S*)-*sec*-buen were obtained in aqueous solution by the usual air-oxidation procedure. To an aqueous solution of $CoCl_2 \cdot 6H_2O$ were added twice the molar amounts of 1,2-diamine, and the resulting solution was aerated for 5 hr at room temperature. Concentrated hydrochloric acid (about 5 ml for 0.01 mol scale) was added, and mixture was evaporated on a water bath until a small amount of green crystals began to separate. To the mixture was added excess perchloric acid (60%), and the green crystals separated were collected and washed with ethanol and ether, and air-dried. The crude products were recrystallized from methanol by adding ether. Found: C, 27.77; H, 6.46; N, 12.71%. Calcd for *trans*-$[CoCl_2((S)\text{-ipren})_2]ClO_4$: C, 27.70; H, 6.51; N, 12.92%. Found:C, 30.93; H, 7.03; N, 11.71%. Calcd for *trans*-$[CoCl_2\ ((S)\text{-}i\text{-buen})_2]ClO_4$: C, 31.22; H, 6.99; N, 12.14%. Found: C, 31.81; H, 7.06; N, 12.24%. Calcd for *trans*-$[CoCl_2((S)\text{-buen})_2]ClO_4$: C, 31.22; H, 6.99; N, 12.14%.

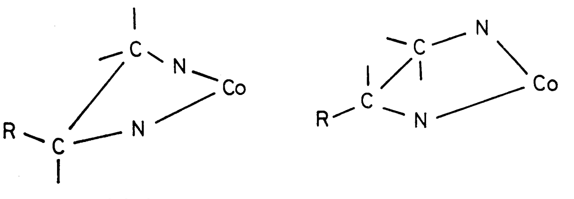
The air-oxidation process was carried out in aqueous methanol and methanol solution for obtaining the (*S*)-benen, (*R*)-phenen complex and $(-)_D$-stien. The subsequent procedures were the same as those mentioned above. Found: C, 39.14; H, 5.66; N, 10.03%. Calcd for *trans*-$[CoCl_2((S)\text{-benen})_2]ClO_4 \cdot H_2O$: C, 39.47; H, 5.52; N, 10.23%. Found: C, 38.54; H, 5.02; N, 11.19%. Calcd for *trans*-$[CoCl_2((R)\text{-phenen})_2]ClO_4$: C, 38.31; H, 4.82; N, 11.17%. Found: C, 53.64; H, 5.46; N, 9.02%. Calcd for *trans*-$[CoCl_2((-)_D\text{-stien})_2]Cl \cdot 2H_2O$: C, 53.73; H, 5.80; N, 8.95%.

Measurements. Visible and ultraviolet absorption spectra were obtained with a Shimadzu MPS 50L recording spectrophotometer. CD spectra were obtained with a JASCO J-20 automatic spectropolarimeter. All the spectra were measured in methanol solution.

Results and Discussion

It has been acknowledged that substituting groups on carbon atoms of puckered 1,2-diamine chelate rings always tend to take the equatorial orientation both in the solid state[13-14] and in solution.[15] Thus, the (*R*)- and (*S*)-pn chelates adopt the δ- and λ-*gauche* conformation, respectively, (Fig. 1), according to the nomenclature of the conformation of a diamine chelate ring based on the proposal in the reference.[16]

The alkyl-substituted 1,2-diamine prepared from (*S*)-amino acid should have the *S* configuration with respect to the asymmetric C atoms of the diamine moiety.. Sor far as the alkyl substituents adopts preferably the equatorial orientation upon coordination, the chelate ring of substituted diamine should have the δ conformation as well as the (*S*)-pn chelate. Since most investigations on the CD of *trans*-dichloro complexes have dealt with the (*R*)-pn or (*S*)-pn complex, we will discuss the CD spectra of our complexes by comparing them with those of the *trans*-$[CoCl_2((R)\text{-pn})_2]^+$ ion or *trans*-$[CoCl_2((S)\text{-pn})_2]^+$ ion.



(a) δ (b) λ

Fig. 1. Conformations of a 1,2-diamine chelate ring: (a) δ-*gauche*; (b) λ-*gauche*.

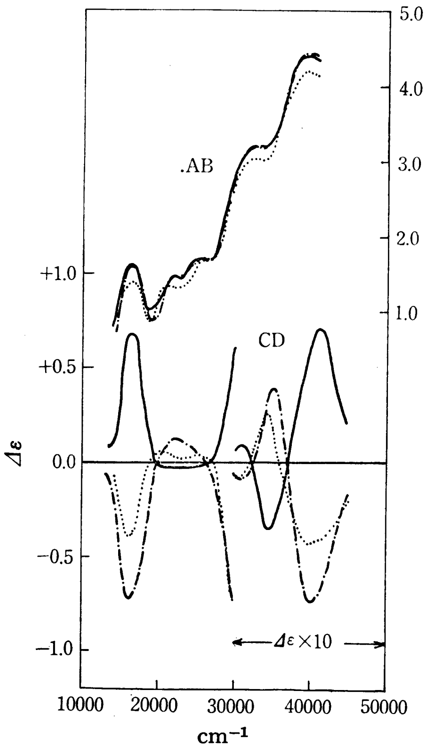


Fig. 2. Absorption (AB) and circular dichroism (CD) spectra of
(—) *trans*-$[CoCl_2((R)\text{-pn})_2]^+$, (···) *trans*-$[CoCl_2((S)\text{-benen})_2]^+$, and (-·-) *trans*-$[CoCl_2((S)\text{-ipren})_2]^+$.

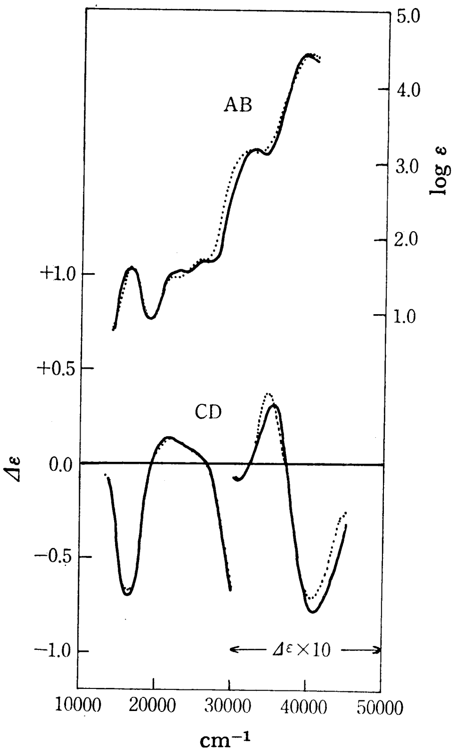


Fig. 3. Absorption (AB) and circular dichroism (CD) spectra of
(—) *trans*-$[CoCl_2((S)\text{-}sec\text{-buen})_2]^+$ and (···) *trans*-$[CoCl_2((S)\text{-}i\text{-buen})_2]^+$.

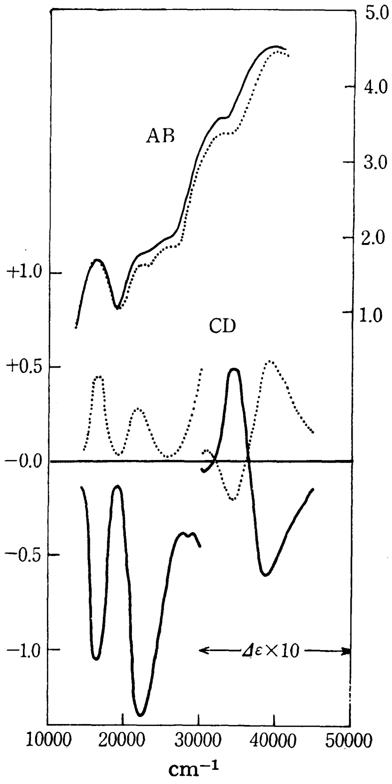


Fig. 4. Absorption (AB) and circular dichroism (CD) spectra of (—) *trans*-$[CoCl_2((-)_D\text{-stien})_2]^+$ and (···) *trans*-$[CoCl_2((R)\text{-phenen})_2]^+$.

CD of C-*Alkylsubstituted 1,2-Diamine Complexes.*

The absorption spectra and circular dichroism spectra are given in Figs. 2—4 and Table 1. The first ligand field transition in the absorption spectrum of cobalt(III) in an octahedral field is ${}^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ which splits in a tetragonal field (*e.g.* *trans*-$[CoCl_2(NH_3)_4]^+$) into ${}^1A_{1g}\rightarrow{}^1E_g(D_{4h})$ and ${}^1A_{2g}(D_{4h})$ component, respectively.17) The band of *trans*-$[CoCl_2(en)_2]^+$ ion at 16000 cm^{-1} was assigned to the ${}^1A_{1g}\rightarrow{}^1E_g(D_{4h})$ transition (I_a), and that at 22000 cm^{-1} to the ${}^1A_{1g}\rightarrow{}^1A_{2g}(D_{4h})$ transition (I_b).17,18) The 1,2-diamine chelate with the λ conformation, such as (*R*)-pn or (*R*)-chxn ((*R*)-chxn= 1(*R*),2(*R*)-diaminocyclohexane), gives a positive and a negative CD band for the I_a band and the I_b band respectively.19)

In the near-ultraviolet and ultraviolet regions, the *trans*-$[CoCl_2(NH_3)_4]^+$ ion gives two strong absorption bands which have been assigned to the charge transfer bands from the halides to the central metal ion, The longer wave length band involving the $p_\pi\rightarrow d_{z^2}$ and the shorter wave length band involving the $p_\sigma\rightarrow d_{z^2}$ transition.20) It was observed that the *trans*-$[CoCl_2((R)\text{-chxn})_2]^+$ ion shows a positive and a negative CD bands for the $p_\pi\rightarrow d_{z^2}$ transition and a positive CD band for the $p_\sigma\rightarrow d_{z^2}$ transition band.21) The (*R*)-pn complex gives a similar CD pattern to that of the (*R*)-chxn complex in the charge transfer region (Fig. 2).32)

As shown in Figs. 2 and 3, the CD spectra of the *trans*-$[CoCl_2((S)\text{-ipren})_2]^+$, *trans*-$[CoCl_2((S)\text{-}i\text{-buen})_2]^+$, *trans*-$[CoCl_2((S)\text{-}sec\text{-buen})_2]^+$ and *trans*-$[CoCl_2((S)\text{-benen})_2]^+$ ion are very similar to each other and to the spectrum of the (*S*)-pn complex (the enantiomorph of (*R*)-pn complex) both in the ligand field and in the charge transfer region. It is apparent from these results that, so far as the methyl, isopropyl, isobutyl, *sec*-butyl and benzyl groups are concerned, the change of the substituting groups on the asymmetric C atom of the diamine chelate makes little contribution to the CD pattern. This means that the optical activity of *trans*-$[CoCl_2(\text{diamine})_2]^+$ system is affected strongly by the conformational contribution and weakly by the vicinal effect.

The (*S*)-*sec*-buen has two asymmetric C atoms, one on the chelate ring and the other in the substituting *sec*-butyl group ((*S*) configuration). A marked resemblance of the CD curves between the (*S*)-*sec*-buen complex

TABLE 1. ELECTRONIC ABSORPTION (AB) AND CIRCULAR DICHROISM (CD) DATA OF *trans*-$[CoCl_2(\text{diamine})_2]^+$ IONS ν IN 10^3 cm^{-1}, (log ε) AND ($\varepsilon_l-\varepsilon_r$)

Diamine	AB	max(log ε)	CD	max ($\varepsilon_l-\varepsilon_r$)
(*R*)-pn	16.50	1.62	16.50	+0.68
	21.97	1.48	21.50	−0.01
	25.97	1.74		
	32.60	3.13	31.15	+0.94
			34.72	−3.60
	39.70	4.40	41.51	+7.01
(*S*)-*i*-buen	16.50	1.60	16.50	−0.67
	21.97	1.48	21.61	+0.14
	25.97	1.71		
	32.78	3.16	30.91	−0.92
			34.72	+3.76
	39.70	4.41	40.65	−7.16
(*S*)-*sec*-buen	16.50	1.61	16.34	−0.71
	22.70	1.53	21.50	+0.13
	26.24	1.74		
	32.78	3.16	30.91	−0.91
			35.08	+3.18
	39.70	4.41	40.65	−7.86
(*S*)-benen	16.50	1.41	16.38	−0.39
	21.97	1.35	20.49	+0.06
	25.97	1.73		
	32.70	3.02	30.76	−0.86
			34.48	+2.47
	39.70	4.17	40.00	−4.26
(*S*)-ipren	16.50	1.61	16.26	−0.73
	22.47	1.48	21.80	+0.12
	25.78	1.71		
	32.70	3.01	30.91	−0.93
			35.08	+3.96
	39.70	4.16	40.32	−7.56
(*R*)-phenen	16.50	1.66	16.26	+0.45
	21.97	1.61	21.50	+0.28
	25.97	1.85		
	32.78	3.37	30.48	+0.58
			34.24	−2.01
	39.70	4.44	38.91	+5.34
(−)-stien	16.50	1.70	16.13	−1.06
	22.98	1.78	21.73	−1.36
	25.97	1.97		
	32.78	3.56	30.03	−0.46
			34.35	+4.98
	39.37	4.52	38.46	−6.10

and the (*S*)-*i*-buen complex (and others) suggests that the additional asymmetric center in the (*S*)-*sec*-buen contributes very little to the CD. This also suggests that the vicinal effect does not contribute much to optical activity.

CD of C-*Phenylsubstituted 1,2-Diamine Complexes.* It has been indicated that the (*R*)-phenen chelate ring has the *λ-gauche* conformation with an equatorially situated phenyl group.[23] The CD pattern of the *trans*-$[CoCl_2((R)\text{-phenen})_2]^+$ ion shown in Fig. 4 obviously differes from that of the (*R*)-pn complex. The (*R*)-phenen complex shows positive maxima both in the I_a and in the I_b region. Both CD peaks have comparable intensities with each other. In the case of the *trans*-$[CoCl_2((R)\text{-pn})_2]^+$ ion, its CD is negative in the I_b and positive in the I_a region. The former CD band is considerably weaker than that of the latter.

Bonich and Harrowfield[2] revealed that the CD sign of the $^1A_{1g}\rightarrow{}^1A_{2g}(D_{4h})$ transition region varies with the change of solvents or the states of the samples (crystal or solution state) in a series of *trans*-$[CoCl_2(1,2\text{-diamine})_2]^+$ complexes, where 1,2-diamines are mono- or disubstituted with alkyl groups. However, a minority of the CD in the A_{2g} transition was still recognized in all cases.[2] The anomalous CD behavior of *trans*-$[CoCl_2((R)\text{-phenen})_2]^+$ ion observed in the first absorption band region would be ascribed to the influence of the phenyl group on the chelate ring.

On the other hand, the CD behavior of the (*R*)-phenen complex resembles closely that of the (*R*)-pn complex in the charge transfer region. This indicates that the phenyl group on the chelate ring has little effect on the CD spectrum in this region. We consider that the CD signs of the charge transfer band region can be regarded as a good indication for determining the conformation of 1,2-diamine chelate rings.

It was found that the CD spectrum of the *trans*-$[CoCl_2((-)_D\text{-stien})_2]^+$ ion, shown in Fig. 4, closely resembles that of the (*R*)-phenen complex, though each corresponding peak has the opposite sign. It is significant that in the charge transfer region, where the phenyl group shows little contribution to determining the CD as described above, both the $(-)_D$-stien and the (*R*)-phenen complexes show the same CD pattern with the opposite signs. This indicates that the $(-)_D$-stein and (*R*)-phenen chelate rings take an antimeric conformation to each other.

The (*R*)-phenen complex should have the *λ* conformation, in which the phenyl group can adopt the equatorial orientation. Hence, the $(-)_D$-stien chelate should have the *δ* conformation. It has been shown that the two phenyl groups of $(-)_D$-stien take the equatorial orientation simultaneously.[23] The absolute configuration of stien satisfies the requirements that the diamine has the *δ* conformation and the equatorial phenyl groups must be of the (*S,S*) configuration.

It has recently been reported that the CD spectra of the Zn(II) complexes of $(-)_D$-stien suggest the (*S,S*) configuration for the ligand in these complexes.[25]

The absolute configuration of $(-)_D$-stien has been assigned to the (*R,R*) configuration,[2,24] based on the examination of the equilibrium between the *Δ* and *Λ* isomers of $[Co((-)_D\text{-stien})_3]^{3+}$ ion, or the exciton analysis of the CD of $(-)_D$-isomarine, the precursor of $(-)_D$-stien. Bosnich and Harrowfield, however, raised some questions on their assignments. Our assignment mentioned above is entirely reverse to these assignments.

If the $(-)_D$-stien has the (*R,R*) configuration, it would be difficult to explain the remarkable difference in CD between the *trans*-dichloro complexes of $(-)_D$-stien and of (*R*)-phenen. On the other hand, if the $(-)_D$-stien has the (*S,S*) configuration, a very significant problem would arise with regard to the assignment of the *Δ* and *Λ* isomers of tris(diamine) complex. Although the true configuration of $(-)_D$-stien should be clarified by X-ray analysis study, we assign the $(-)_D$-stien to the (*S,S*) configuration, since the visible CD curve of the *trans*-$[CoCl_2((-)_D\text{-stien})_2]^+$ ion can be explained by taking into account the vicinal effect of the phenyl group.

By comparing the CD of (*R*)-phenen complex with that of (*R*)-pn complex, it is apparent that the phenyl group affects especially the CD in the I_b ($^1A_{1g}\rightarrow{}^1A_{2g}(D_{4h})$) transition. A strong CD band with negative sign is observed for the *trans*-$[CoCl_2((-)_D\text{-stien})_2]^+$ ion in the I_b region, demonstrating the vicinal effect of the phenyl groups. The visible CD band of the $(-)_D$-stien complex is considerably stronger than that of the (*R*)-phenen complex. This may be due to the difference in the number of phenyl groups between the ligands. The remarkable vicinal effect observed for the phenen, having only one phenyl group, should appear twice as much in the case of stien with two phenyl groups.

It is interesting to note that the (*S*)-benen complex which also has a phenyl group in the ligand shows no obvious influence of the phenyl group in its CD curve. In this case, the phenyl group is separated by a methylene group from the diamine chelate ring. It is suggested, that only the phenyl group attached directly to the 1,2-diamine moiety gives rise to the anomalous vicinal effect in the first absorption band region.

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6) Nomenclature and abbreviations of diamines (abbreviations are given in the parentheses). R=isopropyl; 1,2(*S*)-diamino-3-methylbutane, or (*S*)-*C*-isopropylethylenediamine ((*S*)-ipren). R=isobutyl; 1,2(*S*)-diamino-4-methylpentane, or (*S*)-*C*-(isobutyl)ethylenediamine ((*S*)-*i*-buen). R=*sec*-butyl; 1,2(*S*)-diamino-3(*S*)-methylpentane, or (*S*)-*C*-(*sec*-butyl)ethylenediamine ((*S*)-*sec*-buen). R=benzyl; 1,2(*S*)-diamino-3-phenylpropane, or (*S*)-*C*-benzylethylenediamine ((*S*)-benen). R=phenyl; 1(*R*), 2-diamino-1-phenylethane,

or (*R*)-*C*-phenylethylenediamine ((*R*)-phenen).

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