Optical Resolution of DL-2,2'-Bipiperidine through its Cobalt(III) Complex †

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The separation of racemic 2,2'-bipiperidine and the *meso* form has been performed through the dihydrochloride salt of the diamine. The reaction of racemic 2,2'-bipiperidine with $[Co(NO_2)_6]^{3-}$ has been shown to yield only one DL pair of *trans*-bis(2,2'-bipiperidine)dinitrocobalt(III) complex ion. The dinitro-complex has been characterized and optically resolved using ammonium D-2-bromo-4,7-dimethyl-3-oxobicyclo[2.2.1]heptane-7-methanesulphonate. Optically pure $(-)_{589}$-2,2'-bipiperidine was recovered from the less soluble diastereoisomer and shows a specific rotation of −12.2°. The stereoselective formation of the *trans*-dinitro-complex is discussed in relation to the predictions of strain energy minimization calculations.

The heterocyclic polyamine 2,2'-bipiperidine (bpip) was first synthesized by Blau in 1889.[1] Because of the two asymmetric carbon atoms in 2,2'-bipiperidine, this diamine exists as three isomers, *meso* (*RS*) and a pair of racemic forms, (*RR*) and (*SS*). The stereochemical features mentioned above have not been taken account of previously. Optical resolution of racemic compounds, which has many empirical aspects, is an important area of chemistry. We attempted to resolve racemic bpip by using several resolving agents (L-tartaric acid, dipotassium bis[L-tartrato(4-)-O^1O^2:O^3O^4]diantimonate(III) trihydrate, D-4,7,7-trimethyl-3-oxobicyclo[2.2.1]heptane-2-sulphonic acid, *etc.*), but no tendency to resolve into optical isomers was observed.

Although seven isomers are theoretically possible for *trans*-$[CoX_2(sdmen)_2]^+$ (X = Cl or NO_2, sdmen = *N,N'*-dimethylethylenediamine) ions owing to the asymmetry of the co-ordinated nitrogen centres, we[2] and Tiethof and Cooke[3] prepared *trans*-$[Co(NO_2)_2(sdmen)_2]^+$ and found that the reaction was completely stereoselective, yielding only one DL pair, in which all four *N*-methyl groups have an equatorial arrangement, likely to be the most favourable sterically. The DL pair was successfully resolved into its optical forms with silver D-2-bromo-4,7-dimethyl-3-oxobicyclo[2.2.1]heptane-7-methanesulphonate, AgY. The chelate rings have the same conformation in the active ions. It is generally accepted that the chelate conformations and the orientations of the *N*-alkyl substituents of the chiral diamines will depend on the configuration of the asymmetric carbon atoms.[4] Consequently, it can be expected that *N,N'*-dialkylated DL-diamines react with $[Co(NO_2)_6]^{3-}$ to yield only one racemic pair {*trans*-$[Co(NO_2)_2(D\text{-diamine})_2]^+$ and *trans*-$[Co(NO_2)_2(L\text{-diamine})_2]^+$} stereoselectively which is resolved into its optical isomers. Prompted by this knowledge, we have attempted to resolve racemic bpip into optical isomers through its *trans*-dinitro-complexes.

We report here the procedure for the separation of the racemic isomer and the *meso* isomer of bpip, the optical resolution in detail of the racemic compound through its Co^{III} complex, and the specific rotation of $(-)_{589}$-2,2'-bipiperidine for the first time. Additionally, the stereochemical behaviour toward the Co^{III} ion of the diamine, which seems to be closely related to the optical resolution, is discussed. Recently, the absolute configuration of $(-)_{589}$-2,2'-bipiperidine has been determined as (*RR*) by our *X*-ray structure study of its Co^{III} complex, $(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}\text{-bpip}\}_2]Y\cdot 4H_2O$.[5]

Experimental

Preparation of 2,2'-*Bipiperidine.*—2,2'-Bipyridine was reduced with metallic sodium in ethanol by the method of Krumholz,[6] and the product which is a mixture of *meso* and racemic isomers was collected by steam distillation. The aqueous ethanol solution of the diamine was acidified with hydrochloric acid and evaporated almost to dryness under reduced pressure. The residue was dissolved in a small amount of water and sodium hydroxide pellets were added to the solution carefully. The amine layer separated was extracted with diethyl ether. After evaporation of ether, the free amine was distilled at 16 mmHg (≈2.1 × 10^3 Pa) and 79—81 °C. Up to 73% of the theoretical amount of bpip was recovered in the form of hygroscopic liquid. In the ^1H n.m.r. spectrum of the product, the signals in the range 7.8—8.8 p.p.m., corresponding to the resonance of aromatic protons of 2,2'-bipyridine, were not observed.

Separation of the meso *and Racemic* 2,2'-*Bipiperidine Dihydrochlorides.*—An aqueous solution of the mixture of *meso* and racemic bpip obtained above was treated with an excess of hydrochloric acid and evaporated to dryness under reduced pressure. A suspension of the light brown mixture (110 g) in 95% ethanol (700 cm^3) was heated to boiling, and filtered hot. The insoluble material was treated with ethanol in the same way, the volume of ethanol being adjusted according to the amount of insoluble material. The filtrates were combined and allowed to stand overnight at room temperature. The white fine-needle precipitate, which contained a small amount of prismatic crystals, was removed by filtration. The filtrate was kept at room temperature for a week. The well formed prismatic crystals which separated were collected on a glass filter and washed with absolute ethanol. After evaporation of the filtrate and the washings, the formation of the prismatic crystals was repeated from the 95% ethanol solution several times, and the crystals formed were collected, combined, and recrystallized from absolute ethanol.

From the fine-needle precipitate which was first separated by this procedure, a small amount of the prismatic crystals was removed by recrystallization of the product; this gave only fine-needle crystals. Thus, two bpip dihydrochlorides of differing

† *Supplementary data available* (No. SUP 56175, 44 pp.): ^{13}C n.m.r. and i.r. spectra of *rac*-bpip and *meso*-bpip dihydrochlorides, strain energy minimization data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.
Non-S.I. unit employed: cal = 4.184 J.

stereochemistry were obtained. The less soluble dihydrochloride which forms fine-needle crystals can be assigned to the *meso* isomer; the more soluble one, crystallized as well formed prisms of the racemic compound, is discussed below. The purity of the dihydrochlorides was examined by ^{13}C n.m.r. spectra in D_2O. The *meso* and racemic isomers of 2,2′-bipiperidine, consequently, were easily separated as the dihydrochlorides (Found for *meso* isomer: C, 49.6; H, 8.90; N, 11.2. Found for racemic isomer: C, 49.5; H, 9.05; N, 11.5. $C_{10}H_{22}Cl_2N_2$ requires C, 49.8; H, 9.20; N, 11.6%).

The dihydrochlorides were converted into the free amines by a similar method (extraction with ether, evaporation of ether, distillation of amine) to that for the mixture of *meso* and racemic amine described above.

Reaction of Racemic 2,2′-Bipiperidine with $Na_3[Co(NO_2)_6]$: *Preparation of trans-*$[Co(NO_2)_2(rac\text{-bpip})_2]NO_2\cdot 0.5H_2O$.—To an aqueous solution of $Na_3[Co(NO_2)_6]$ (21.0 g) was added dropwise with stirring racemic 2,2′-bipiperidine (*rac*-bpip) (20.0 g), obtained as above, and the solution was heated on a water-bath for 1 h at 60 °C. After cooling, the yellow precipitates which separated were filtered off, washed with ice-cold water, and air-dried; yield 21.4 g. The yellow precipitates were recrystallized from a minimum amount of warm water and the resulting crystals were filtered off, washed with ice-cold water, and dried under vacuum. All fractions precipitated were identified as the *trans*-$[Co(NO_2)_2(rac\text{-bpip})_2]^+$, which consists of *trans*-$[Co(NO_2)_2\{(RR)\text{-bpip}\}_2]^+$ and *trans*-$[Co(NO_2)_2\{(SS)\text{-bpip}\}_2]^+$, by their ^{13}C n.m.r. spectra. Thus, no evidence for other isomers was obtained (Found: C, 44.3; H, 7.35; N, 18.1. $C_{20}H_{41}CoN_7O_{6.5}$ requires C, 44.3; H, 7.60; N, 18.1%)

Resolution of 2,2′-Bipiperidine: Preparation of $(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}\text{-bpip}\}_2]Y\cdot 4H_2O$.—*trans*-$[Co(NO_2)_2(rac\text{-bpip})_2]NO_2\cdot 0.5H_2O$ (20.0 g) was dissolved in water (100 cm^3) and heated on a water-bath at 60 °C. To the warm solution was added ammonium D-2-bromo-4,7-dimethyl-3-oxobicyclo[2.2.1]heptane-7-methanesulphonate, NH_4Y (12.3 g); the mixture was filtered after sufficient stirring to dissolve the resolving agent. The filtrate was allowed to stand overnight in a refrigerator. The resulting needle-like yellow crystals were collected, washed with a small amount of ice-cold water, and air-dried. Repeated recrystallizations were performed from water at 55 °C until values of the ratio α (435 nm)/ε (absorption coefficient) became constant for the filtrate; yield 6.1 g (after three recrystallizations) (Found: C, 41.7; H, 7.65; N, 9.65. $C_{30}H_{62}BrCoN_6O_{12}$ requires C, 41.5; H, 7.20; N, 9.65%).

Recovery of $(-)_{589}$-*2,2′-Bipiperidine from the Cobalt*(III) *Complex*.—$(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}\text{-bpip}\}_2]Y\cdot 4H_2O$ (5.6 g) was dissolved in water (500 cm^3) with sonicated stirring. The solution was poured into a column (60 × 4 cm) containing an anion-exchange resin (QAE-Sephadex, NO_2^- form). The column was flushed with water to elute the yellow complex thoroughly. The eluted solution was collected and evaporated under reduced pressure to give a thick syrup; this was dried under vacuum overnight. The resulting yellow powder was collected mechanically, and used in the next step without further purification; yield 4.2 g. A part of the powder was recrystallized to obtain $(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}\text{-bpip}\}_2]NO_2$ (see below).

Sodium sulphide nonahydrate (20.0 g) and KOH (4.0 g) were fused at 80 °C. The yellow powder obtained above (4.0 g) was poured onto the fused mass, and NaOH (50.0 g) was added to the mixture. The black mixture was heated for a few minutes at 100 °C. Benzene (100 cm^3) was then added and refluxed for 30 min. After cooling, the benzene solution was decanted onto KOH pellets and the extraction was repeated with a fresh portion (100 cm^3) of benzene. $(-)_{589}$-2,2′-Bipiperidine was then extracted with concentrated hydrochloric acid from the brown benzene solution. The acidic aqueous layer was separated and evaporated under reduced pressure, so the dihydrochloride was obtained as a pale yellow powder. An aqueous solution of the bpip dihydrochloride was treated with NaOH and the free amine was re-extracted with ether. The ether layer was separated, dried on KOH pellets for 3 d, and removed by distillation. $(-)_{589}$-2,2′-Bipiperidine was recovered as an almost colourless solid at room temperature; yield 580 mg, m.p. 34.2 °C.

The specific rotation of $(-)_{589}$-2,2′-bipiperidine (0.1 g) was determined as follows: $(-)_{589}$-2,2′-bipiperidine was dissolved in water (10 cm^3), and the bpip concentration of the solution was exactly determined by titration with 0.1 mol dm^{-3} perchloric acid solution; α(589 nm, 18 °C, 0.092 g cm^{-3} in H_2O) = − 12.2°.

Strain Energy Minimization Calculations.—The minimized strain energies of the complexes *trans*-$[Co(NH_3)_2\{(RR)\text{-bpip}\}_2]^+$ and *trans*-$[Co(NH_3)_2\{(RR)\text{-bpip}\}\{(SS)\text{-bpip}\}]^+$ were calculated using the program CONFAN 2 developed by Yamaguchi *et al.*[7] The trial co-ordinates for each complex ion were generated from our previous *X*-ray study of $(-)_{546}$-*trans*-$[Co(NO_2)_2\{(RR)\text{-bpip}\}_2]Y\cdot 4H_2O$.[5] All calculations were performed on a HITAC 8700/8800 computer at this university.

Results and Discussion

Separation and Assignment of the meso *and Racemic* 2,2′-*Bipiperidine*.—In some cases, diamines having two amino-groups bonded to the adjacent asymmetric carbon centres have been separated into their *meso* and racemic isomers, through their dihydrochlorides, using fractional recrystallization.[8] Aqueous ethanol solution is usually employed and it is also suitable for the separation of *meso* and racemic bpip. The dihydrochloride salt of the mixture of *meso* and racemic bpip was obtained from the starting material which was synthesized by the reduction of 2,2′-bipyridine. The ^{13}C n.m.r. spectrum in D_2O of the dihydrochloride salt shows ten signals. On the other hand, each spectrum of the less and more soluble isomer after the separation of the dihydrochloride salt from ethanol gives five different signals. Therefore the purity of these isomers can be examined by their ^{13}C n.m.r. spectra, though their assignment was difficult at this stage. In the spectra using the Gated-I technique, the highest-field peak of each isomer is a doublet and the other signals are triplets. Thus, the methine carbon absorptions can be assigned to the signals at 59.4 and 59.1 p.p.m. for the less and more soluble isomer, respectively. The other signals observed at lower field, consequently, correspond to the remaining methylene resonances. Thus, the two isomers can be distinguished by their ^{13}C n.m.r. spectra in D_2O; they appear to be produced in roughly equal amounts.

The less soluble isomer which forms as fine-needle crystals gave a simpler i.r. spectrum than the more soluble one. In the *meso* structure of bpip the sole molecular symmetry element, the mirror plane, is coincident with the perpendicular plane between the two asymmetric carbon centres. It is, therefore, expected that the i.r. spectrum of the *meso* isomer is simpler than that of the racemic isomer, so that the less soluble fine-needle crystals obtained can be assigned to the dihydrochloride of *meso*-bpip. This tentative assignment was confirmed by the optical resolution of racemic bpip, whose dihydrochloride crystallized in the form of prisms, as its Co^{III} complex.

Preparation and Structure of the Complexes.—The inactive *trans*-dinitro-complex *trans*-$[Co(NO_2)_2(rac\text{-bpip})_2]NO_2\cdot 0.5H_2O$ was prepared by the reaction of racemic 2,2′-bipiperidine,

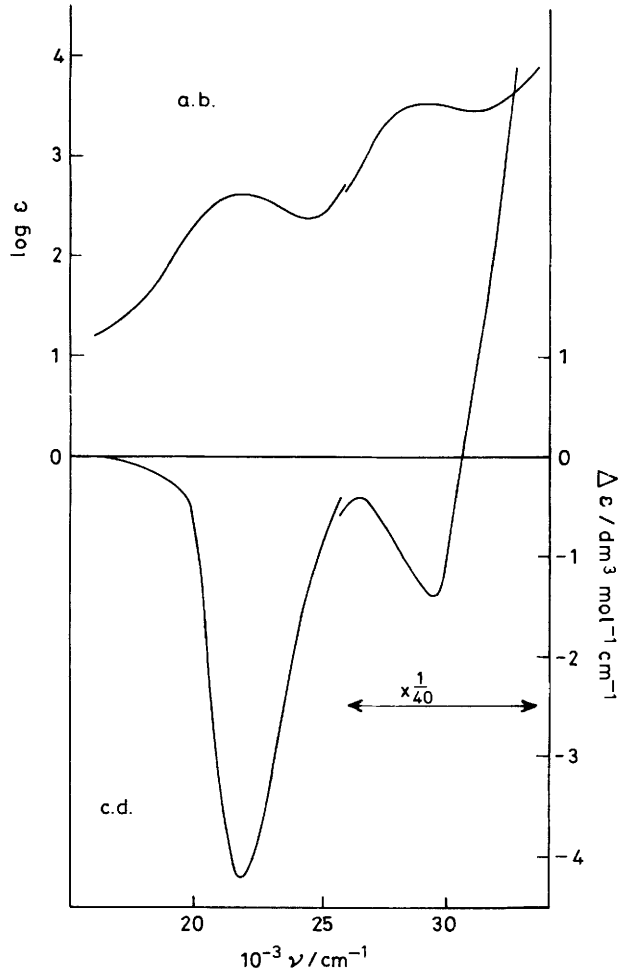

Figure. The a.b. and c.d. spectra of *trans*-$[Co(NO_2)_2\{(-)\text{-bpip}\}_2]^+$ in $HClO_4$ (0.01 mol dm^{-3}) solution

whose dihydrochloride forms the prismatic crystals from ethanol, with $Na_3[Co(NO_2)_6]$. This substitution has been employed previously to obtain *trans*-dinitro-complexes of this type.[9] This reaction gave the crystals composed of a single species (confirmed by ^{13}C n.m.r.), though the enantiomeric isomers must necessarily be present in equal amounts, in high yield (75.8%). The absorption (a.b.) and circular dichroism (c.d.) spectra of *trans*-$[Co(NO_2)_2\{(-)\text{-bpip}\}_2]^+$ are shown in the Figure. The spectral data are summarized in Table 1, together with those of the resolved complexes $(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}\text{-bpip}\}_2]Y\cdot 4H_2O$ and $(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}\text{-bpip}\}_2]NO_2$, the counter ion in the former being converted into nitro-anion to give the latter. It is generally acknowledged that the absorption spectra of cobalt(III) diamine diacid complexes are characteristic of their geometry.[10] It is recognized that bis(diamine)dinitro-complexes of Co^{III} show $\lambda_{max.}$ at *ca.* 330 nm for the *cis* isomers and at *ca.* 350 nm for the *trans* isomers. The present complexes show $\lambda_{max.}$ at 345 nm in H_2O; this indicates that they have the *trans* configuration with respect to the two nitro-groups. In the ^{13}C n.m.r. spectra of the complexes, which contain 20 carbon atoms in each complex ion, only five signals were observed except for the optically active complex involving the anion Y^- (which also has signals due to Y^-). These results require that the four piperidine rings in each *trans*-dinitro-complex are chemically equivalent in D_2O. This structural assignment of the *trans*-dinitro-complexes can be compared with our previous *X*-ray structure determination of

Table 1. The a.b. and c.d. spectra of $(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}\text{-bpip}\}_2]^+$

	Absorption		Circular dichroism	
Counter ion*	$\lambda_{max.}$/nm	log(ε/dm^3 mol^{-1} cm^{-1})	λ/nm	Δε/dm^3 mol^{-1} cm^{-1}
NO_2^-	460	2.63	456	−4.18
	345	3.55	328	0
Y^-	460	2.55	455	−3.63
	346	3.46	329	0

* Y^- = D-2-bromo-4,7-dimethyl-3-oxobicyclo[2.2.1]heptane-7-methanesulphonate.

the complex $(-)_{546}$-*trans*-$[Co(NO_2)_2\{(-)_{589}\text{-bpip}\}_2]Y\cdot 4H_2O$.[5] The similarity in their ^{13}C n.m.r. spectra is significant.

In the case of optically active pipecolic acid (2-piperidinecarboxylic acid), whose stereoselective co-ordination to a Co^{III} ion has been observed,[11] the piperidine ring is considered to be adopting a chair form in order to minimize the steric interaction with axial ligands. Accordingly, the ring conformation of the co-ordinated racemic 2,2′-bipiperidine can be regarded as a chair form, owing to its cyclic structure. Thus, there are three possible structures of *trans*-$[Co(NO_2)_2(rac\text{-bpip})_2]^+$, obtained by the substitution reaction with $[Co(NO_2)_6]^{3-}$: a racemic pair of *trans*-$[Co(NO_2)_2\{(RR)\text{-bpip}\}_2]^+$ and *trans*-$[Co(NO_2)_2\{(SS)\text{-bpip})_2]^+$, and a *meso* isomer *trans*-$[Co(NO_2)_2\{(RR)\text{-bpip}\}\{(SS)\text{-bpip}\}]^+$. According to the structural assignment described above, the complex *trans*-$[Co(NO_2)_2(rac\text{-bpip})_2]^+$ obtained is composed of *trans*-$[Co(NO_2)_2\{(RR)\text{-bpip}\}_2]^+$ and *trans*-$[Co(NO_2)_2\{(SS)\text{-bpip}\}_2]^+$, where the enantiomeric isomers must necessarily be present in equal amounts. Consequently, the substitution reaction occurs stereoselectively allowing the possibility of optical resolution of racemic bpip through its *trans*-dinitrocobalt(III) complex. In fact, the optical resolution of this complex was attained using the resolving agent NH_4Y from its aqueous solution. It is important that the formation of the *meso* complex *trans*-$[Co(NO_2)_2\{(RR)\text{-bpip}\}\{(SS)\text{-bpip}\}]^+$ should be excluded. This stereoselective behaviour of racemic 2,2′-bipiperidine toward Co^{III} ion is discussed in the following section.

Strain Energy Minimization.—As described above, it is remarkable that the formation of the *trans*-dinitro-complex containing racemic bpip occurs stereoselectively. The technique of strain energy minimization calculation was, therefore, applied to optically active *trans*-$[Co(NH_3)_2\{(RR)\text{-bpip}\}]^{3+}$ and inactive *trans*-$[Co(NH_3)_2\{(RR)\text{-bpip}\}\{(SS)\text{-bpip}\}]^{3+}$, where both complexes were assumed to be good models for the corresponding *trans*-dinitro complexes.

Minimization of the total strain energy was achieved by using a Broyden-Fletcher-Shanno variable metric method.[12] The final energy terms are listed in Table 2.

The optically active complex *trans*-$[Co(NH_3)_2\{(RR)\text{-bpip}\}_2]^{3+}$ has the less strained structure, there being a large difference between the total strain energies of the active and inactive isomers. Significant contributions to the energy difference come from the bond-length strains, angle deformations, and non-bonded interactions. The difference in the strain energy due to the Co–N bond extension is almost comparable with that of the total bond-length strain energy involving the bpip moieties. Furthermore, the angle deformations around the cobalt atom contribute significantly to the bond-angle strain energy and its difference. In the inactive complex ion, larger

Table 2. Final energy terms (kcal mol^{-1})

Strain energy	(*RR*)–(*RR*)[a]	(*RR*)–(*SS*)[b]	S.e.d.[c]
Bond length	3.74	7.52	3.78
Bond angle	12.59	21.36	8.77
Torsional	1.45	1.63	0.18
Non-bonded	3.53	8.99	5.46
Out-of-plane	0.00	0.00	0.00
Total	21.31	39.50	18.19

[a] Optically active *trans*-$[Co(NH_3)_2\{(RR)\text{-bpip}\}_2]^{3+}$ ion. [b] Optically inactive *trans*-$[Co(NH_3)_2\{(RR)\text{-bpip}\}\{(SS)\text{-bpip}\}]^{3+}$ ion. [c] Strain energy difference: s.e.(*RR*)–(*SS*) − s.e.(*RR*)–(*RR*).

Table 3. Significant non-bonded interactions

	Strain energy* (distance/Å)	
	(*RR*)–(*RR*)	(*RR*)–(*SS*)
C(5) ··· H(40)	0.06 (2.71)	1.08 (2.32)
H(9) ... H(40)	−0.02 (3.65)	1.06 (2.01)
H(10) ··· H(40)	0.83 (2.06)	1.58 (1.93)
C(10) ··· H(30)	0.09 (2.67)	1.02 (2.33)
H(19) ··· H(30)	−0.02 (3.61)	0.74 (2.08)
H(20) ··· H(30)	1.04 (2.01)	2.06 (1.87)

* In kcal mol^{-1}.

angular distortions of the N–Co–N angles are produced. Moreover, the angle deformations associated with the methylene groups connected to the asymmetric nitrogen atoms significantly contribute to the energy difference.

The energy difference of the intra-ring interactions of the four piperidine rings is almost negligible. On the other hand, the significant large repulsive contacts between the neighbouring methylene groups linked to the amino groups appears to cause a significantly large energy difference. These close contacts in each complex ion are summarized in Table 3. Such intramolecular interactions may be reduced by the bond extensions and angle deformations around the cobalt atom mentioned above, especially in the optically inactive complex ion.

According to the clarified significant effects of the adjacent methylene groups linked to the amino groups, the stereoselective formation of the *trans*-$[Co(NO_2)_2(rac\text{-bpip})_2]^+$ complex, which gives rise to a possible route optically to resolve 2,2′-bipiperidine through the complex, can be deduced from the calculations carried out on the corresponding diamine complexes. It can also be expected that racemic diamines analogous to 2,2′-bipiperidine, which have symmetrical structures with *N*-alkyl groups forming a five-membered chelate to the cobalt(III) ion, can be optically resolved.

Conclusions

2,2′-Bipiperidine possesses two asymmetric carbon atoms and is therefore found in two forms, racemic and *meso*. In this work, the separation of the racemic and *meso* forms was first attained from aqueous ethanol solutions of their dihydrochlorides. Moreover, a novel procedure was contrived by employing the co-ordination toward Co^{III} ion. Namely, racemic *trans*-bis(2,2′-bipiperidine)dinitrocobalt(III) ion, which was obtained by the substitution reaction of $[Co(NO_2)_6]^{3-}$ with racemic 2,2′-bipiperidine and has no net chirality around the Co^{III} ion, was optically resolved.

The substitution reaction, consequently, occurred to give only one racemic form without the *meso* form *trans*-$[Co(NO_2)_2\{(RR)\text{-bpip}\}\{(SS)\text{-bpip}\}]^+$, allowing the possibility of optical resolution of racemic 2,2′-bipiperidine through the *trans*-dinitro-complex. This stereoselective formation of *trans*-$[Co(NO_2)_2(rac\text{-bpip})_2]^+$ plays an important role in the resolution of 2,2′-bipiperidine. Conformational analysis studies, in order to account for the stereoselectivity, of models of these two forms (racemic and *meso*) are consistent with experimental results and show that the difference in stability is 18.2 kcal mol^{-1}. The difference arises because of significant energy contributions from the interatomic interactions among the *N*-alkyl (methylene) groups on neighbouring 2,2′-bipiperidine co-ordinated to the same Co^{III} ion. Thus, the present procedure for the optical resolution will be applicable to other racemic *N*-alkyl-substituted diamines.

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References

1 F. Blau, *Monatsh. Chem.*, 1889, **10**, 375.
2 S. Yano, M. Saburi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 3486.
3 J. A. Tiethof and D. W. Cooke, *Inorg. Chem.*, 1972, **11**, 315.
4 T. Makino, S. Yano, and S. Yoshikawa, *Inorg. Chem.*, 1979, **18**, 1048.
5 M. Sato, Y. Sato, S. Yano, S. Yoshikawa, K. Toriumi, H. Itoh, and T. Itoh, *Inorg. Chem.*, 1982, **21**, 2360.
6 P. Krumholz, *J. Am. Chem. Soc.*, 1953, **75**, 2163.
7 M. Yamaguchi, S. Yamamatsu, T. Furusawa, S. Yano, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, 1980, **19**, 2010; M. Yamaguchi, S. Yano, M. Saburi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 691.
8 T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1970, 9, 1807; F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 3051.
9 H. F. Holtzclaw, jun., D. P. Sheetz, and B. D. McCarty, *Inorg. Synth.*, 1953, **4**, 176.
10 H. Kuroya and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, 1940, **15**, 427; M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, 1951, **266**, 49; 1951, **267**, 113; 1952, **271**, 101.
11 M. Saburi and S. Yoshikawa, *Inorg. Chem.*, 1968, **7**, 1890.
12 R. W. H. Sargent and B. A. Murtagh, *Computer J.*, 1970, **13**, 185.

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