Chiral Metal Complexes.
10.* The Inversion of Λ-α-{dichloro[3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane]cobalt(III)} to a Δ-β Isomer via an Isolated Δ-β-Dinitro Intermediate

JILL A. CHAMBERS, MOH'D W. MULQI, PETER A. WILLIAMS**

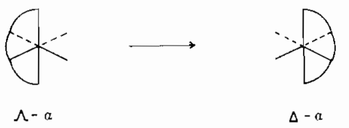
Department of Chemistry, University College, P.O. Box 78, Cardiff CF1 1XL, U.K.

and ROBERT S. VAGG**

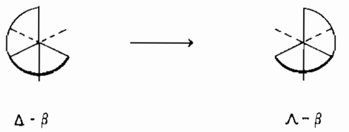
School of Chemistry, Macquarie University, North Ryde 2113, N.S.W., Australia

Received April 7, 1983

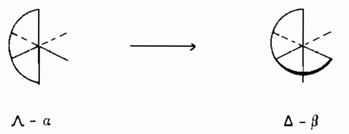
*Λ-α-{Dichloro[3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane]cobalt(III)}, Λ-α[Co(*R*-picpn)Cl_2]$^+$, reacts with nitrite ion in aqueous solution, inversion occurs and the main product is Δ-β-[Co(*R*-picpn)(NO_2)$_2$]$^+$. This reaction is stereospecific in that only one of four possible Δ-β isomers forms. A small amount of Λ-α-[Co(*R*-picpn)(NO_2)$_2$]ClO_4 was isolated from the reaction solution. The Λ-α-diastereomer readily isomerizes to the favoured Δ-β form, the reaction being light-catalysed. Reaction of the isolated Δ-β-dinitro species with concentrated hydrochloric acid results in the stereospecific formation of one isomer of Δ-β-[Co(*R*-picpn)Cl_2]$^+$. All of the complexes were investigated using circular dichroism and high resolution proton NMR methods.*



(*1*)



(*2*)



(*3*)

Introduction

Proven inversion of absolute configuration at the metal centre in octahedral coordination complexes is uncommon. In species which contain a linear tetradentate two kinds of inversion may be envisaged. The first, shown in (*1*), represents a complete inversion of the α-coordination geometry and, to our knowledge, only one example has been reported [1]. Related to this kind of stereochemical change is the somewhat analogous interconversion of β isomers represented in (*2*). An example of this kind of inversion was observed by Job [2] who carried out the reaction (*4*)‡ in alcoholic solution, where pro is the prolinate anion.

$$\Lambda\text{-}\beta\text{-}[\mathrm{Co}(2S,9S\text{-dimetrien})(S\text{-pro})]^{2+} \xrightarrow{\mathrm{EtOH}} \Delta\text{-}\beta\text{-}[\mathrm{Co}(2S,9S\text{-dimetrien})(S\text{-pro})]^{2+} \quad (4)$$

The thermodynamic and steric reasons for this asymmetric transformation have been elegantly outlined by previous workers [3] using the related trien complex. Another comparable and unusual isomerization

---

*Part 9 is ref. [1].

**Authors to whom correspondence should be addressed.

‡2,9-dimetrien = 2,9-diamino-4,7-diazadecane, proH = proline, trien = 1,4,7,10-tetraazadecane, *R*-picpn = 3*R*-methyl-2,6-di(2-pyridyl)-2,5-diazahexane, 3,8-dimetrien = 3,8-dimethyl-1,4,7,10-tetraazadecane, 5-metrien = 5-methyl-1,4,7,10-tetraazadecane, en = 1,2-diaminoethane, ox = oxalate dianion.

0020-1693/84/$3.00

process involving the transformation Λ-α to Λ-β (*5*) is also known [2, 4–6]:

$$\Lambda\text{-}\alpha\text{-}[\mathrm{Co}(2S,9S\text{-dimetrien})\mathrm{Cl}_2]^+ \xrightarrow{S\text{-aaH}} \Lambda\text{-}\beta\text{-}[\mathrm{Co}(2S,9S\text{-dimetrien})(S\text{-aminoacidate})]^{2+} \qquad (5)$$

The reaction is thought to proceed *via* a square-planar intermediate [2].

However, the most frequently encountered octahedral inversion is that shown in (*3*) and which has been described as involving an edge displacement in the coordination sphere [7]. Such a stereochemical change was first found [8–10] during the base hydrolyses of both Λ-α-$[\mathrm{Co(trien)Cl_2}]^+$ and Λ-α-$[\mathrm{Co(trien)(OH)Cl}]^+$. Subsequently several analogous reactions of complexes of Co(III) have been reported, all involving substitution in the coordination sphere [2, 5, 11, 12].

One such inversion occurs when the complex Λ-α-$[\mathrm{Co}(2S,9S\text{-dimetrien})\mathrm{Cl_2}]^+$ is reacted with $\mathrm{Li_2CO_3}$ (when the inversion presumably takes place), then acid and nitrite ion, to yield a mixture of Δ-β-$[\mathrm{Co}(2S,9S\text{-dimetrien})(\mathrm{NO_2})_2]^+$ and Δ-β-$[\mathrm{Co}(2S,9S\text{-dimetrien})(\mathrm{ONO})\mathrm{NO_2}]^+$, [5]. Recently we reported [1] that when Λ-α-$[\mathrm{Co}(R\text{-picpn})\mathrm{Cl_2}]^+$ reacts with oxalate ion in aqueous solution, total inversion occurs to yield Δ-α-$[\mathrm{Co}(R\text{-picpn})(\mathrm{ox})]^+$. A related dinitro species, $[\mathrm{Co(picpn)(NO_2)_2}]^+$ is known [13, 14], which, when prepared from Λ-α-$[\mathrm{Co}(R\text{-picpn})\mathrm{Cl_2}]^+$ or its enantiomer, is said [14] to retain the geometry and absolute configuration of its parent cationic complex.

We wish to report in this paper that under certain conditions inversion occurs in this reaction, (*6*). It is possible to isolate Λ-α-$[\mathrm{Co}(R\text{-picpn})(\mathrm{NO_2})_2]\mathrm{ClO}_{4(s)}$, from reaction mixtures as a least soluble

$$\Lambda\text{-}\alpha\text{-}[\mathrm{Co}(R\text{-picpn})\mathrm{Cl_2}]^+ \xrightarrow{\mathrm{NO_2}^-} \Delta\text{-}\beta\text{-}[\mathrm{Co}(R\text{-picpn})(\mathrm{NO_2})_2]^+ \qquad (6)$$

diastereoisomer but the cation inverts stereospecifically to one of the four possible Δ-β isomers in aqueous solution. The Δ-β product may then be reacted further to yield, stereospecifically, one isomer of Δ-β-$[\mathrm{Co}(R\text{-picpn})\mathrm{Cl_2}]^+$.

Experimental

Microanalyses were carried out by Mrs. A. Dams in the Department of Chemistry, Cardiff. Electronic and circular dichroism spectra were recorded using a Pye-Unicam SP8000 spectrophotometer and a Jobin-Yvon CNRS Dichrographe III, respectively. 360 MHz ^{1}H nmr spectra were obtained at 298 K using a Bruker WM-360 instrument. Spectra were recorded in 10:1(v/v) $\mathrm{D_2O}$:$\mathrm{d_4}$-MeOH and chemical shifts are reported using the $\mathrm{d_3}$-MeOH impurity as internal standard (δ 3.30 ppm), or in $\mathrm{d_6}$-DMSO using its $\mathrm{d_5}$-impurity resonance at 2.62 ppm as the internal standard. Infrared spectra in nujol mulls were obtained using a Perkin Elmer 257 spectrometer.

Λ-α-[Co(R-picpn)Cl$_2$]ClO$_4$

This complex was prepared as described previously [1].

[Co(R-picpn)(NO$_2$)$_2$]ClO$_4$

The compound was prepared using a method akin to that of Bosnich and Kneen [15]. To a suspension of Λ-α-$[\mathrm{Co}(R\text{-picpn})\mathrm{Cl_2}]\mathrm{ClO_4}$ (1.00 g, 1.99 mmol) in $\mathrm{H_2O}$ (30 cm^3) was added sodium nitrite (0.274 g, 3.97 mmol) and the reaction mixture was heated on a water bath for 30 min during which time all the solids dissolved to yield a deep yellow solution. This was filtered into an aqueous solution (10 cm^3) of sodium perchlorate hydrate (3 g). The resulting solution was cooled in an ice bath for an hour, over which time a deep yellow crystalline precipitate deposited. This was collected at the pump, washed with ice water and air-dried. Yield: 0.48 g. *Anal.* Found: C, 35.5; H, 3.7; N, 16.6%. Calc. for $\mathrm{C_{15}H_{20}N_6O_8ClCo}$: C, 35.6; H, 4.0; N, 16.6%. After cooling the filtrate for a further 3 hours in an ice bath, a second fraction was isolated as above. Yield: 0.20 g. *Anal.* Found: C, 35.5; H, 3.8; N, 16.7%. The filtrate was placed in a desiccator over silica gel and slowly evaporated under reduced pressure. During the next week, three more crops of yellow crystals were isolated which had CD spectra identical to that of the second fraction and gave the same analytical results (Yield: 0.28 g. Total yield: 0.96 g, 95.4%). The remaining filtrate had the same CD spectrum (identical null dichroic wavelengths and proportional rotatory strengths of all bands) as the later crops of solid complex.

Δ-β-[Co(R-picpn)Cl$_2$]ClO$_4$·2H$_2$O

Portions of Δ-β-$[\mathrm{Co}(R\text{-picpn})(\mathrm{NO_2})_2]\mathrm{ClO_4}$ (see below) were placed in an evaporating basin and treated with concentrated hydrochloric acid. The resultant red-purple solutions were evaporated to dryness on a steam bath to yield the Δ-β-dichloro complex quantitatively. *Anal.* Found: C, 34.7; H, 4.4; N, 10.6%. Calc. for $\mathrm{C_{15}H_{24}N_4O_6Cl_3Co}$: C, 34.5; H, 4.6; N, 10.7%.

Results and Discussion

The infrared spectrum of each crop of dinitro product indicated that no *O*-bonded nitrito species is present [16, 17], and the ir spectra of all but the first crop were identical. High resolution ^{1}H nmr

TABLE I. 360 MHz ^{1}H NMR Data[a] for the Complexes.

	Δ-β-[Co(*R*-picpn)(NO$_2$)$_2$]$^+$ [b]		Δ-β-[Co(*R*-picpn)Cl$_2$]$^+$ [c]	
H(3)	d[d]	7.54	d	7.81
H(4)	t	8.22	t	8.39
H(5)	t	7.80	t	8.14[f]
H(6)	d	8.91	d	9.40
H(3′)	d	7.66	d	7.98
H(4′)	t	8.08	t	8.14[f]
H(5′)	t	7.44	t	7.48
H(6′)	d	7.20	d	6.98
H(31)	m	3.18[e]	m	2.80
H(41)	t(dd)	4.11	t(dd)	3.55
H(42)	dd	3.15[e]	dd	3.26
CH_3	d	1.33	d	1.29
J_{31,CH_3}		5.59		5.80
$J_{31,41}$		13.06		12.80
$J_{31,42}$		3.58[e]		4.23
$J_{41,42}$		−13.49		−12.13

[a] Chemical shifts ± 0.01 ppm, coupling constants ± 0.05 Hz. [b] In D_2O:CD_3OD 10:1 (v/v) at 298 K. [c] In d_6-DMSO at 298 K. [d] d = doublet, t = triplet, m = multiplet, dd = doublet of doublets. [e] Coupling constants and chemical shifts deduced from irradiation experiments. [f] These signals overlap.

TABLE II. Electronic and CD Spectral Data for the Complexes.

Complex	10^{-3} ϵ/dm^2 mol^{-1} [a]	$\Delta\epsilon$/dm^2 mol^{-1} [a]
[Co(*S*-picpn)(NO$_2$)$_2$]ClO$_4$ [b]	3.61(445)	−13.5(456)
		+20.7(335)
[Co(*R*-picpn)(NO$_2$)$_2$]$^+$ [c]	3.00(444)	+20.0(456)
Λ-α-[Co(*R*-picpn)(NO$_2$)$_2$]ClO$_4$ [d]	3.01(445)	+16.8(457)
	50.9(333)	−27.8(334)
	277.3(248)	+50.3(272)
		−83.4(257)
Δ-β-[Co(*R*-picpn)(NO$_2$)$_2$]ClO$_4$ [d]	3.05(445)	−10.4(467)
	57.9(333)	+10.2(417)
	273.3(246)	−16.1(362)
		+33.5(325)
		+19.0(284)
Δ-β-[Co(*R*-picpn)Cl$_2$]ClO$_4$·2H$_2$O [e]	1.69(530)	+4.6(579)
	10.7(339)[f]	−7.6(509)
	234.2(254)	−2.1(424)
		+5.0(371)
		−54.5(281)
		+156.3(261)

[a] Figures in brackets refer to λ_{max} (nm) for electronic spectra and extrema in the CD spectra. [b] From ref. [14]; CD data taken from Fig. 1. Spectrum measured in MeOH. [c] From ref. [13]; Electronic and CD data taken from Fig. 1. Solvent not given. [d] Spectra measured in H_2O solution at 298 K. [e] Spectra measured in conc. HCl solution at 298 K. [f] Shoulder.

spectra (Table I) showed that only one isomer was present in this material, demonstrated by the presence of only one doublet corresponding to the methyl group of the picpn ligand. All resonances in the aromatic region were well resolved and could be assigned using spin-decoupling techniques. Four doublets and four triplets were evident each of which integrated for one proton. Of central importance is

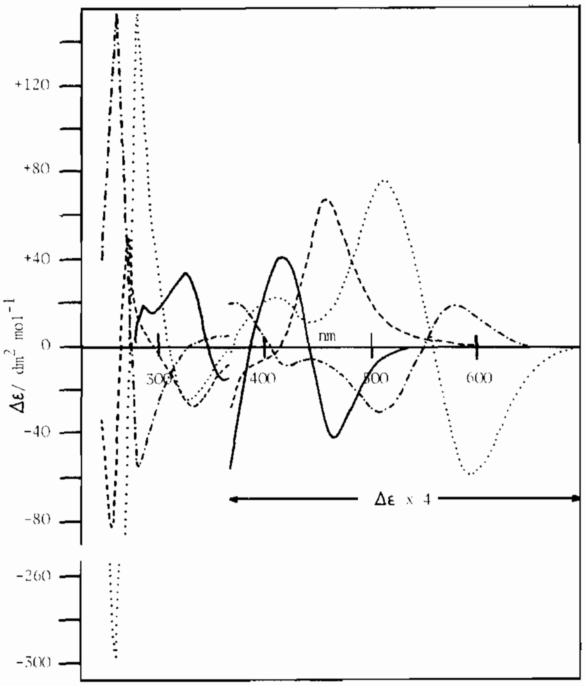
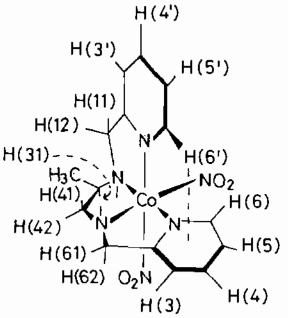
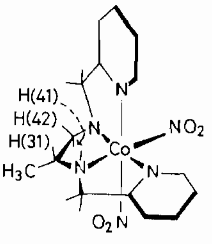


Fig. 1. CD spectra of (——) Δ-β-[Co(*R*-picpn)$(NO_2)_2$]$^+$ and (-----) Λ-α-[Co(*R*-picpn)$(NO_2)_2$]$^+$ in aqueous solution and (·····) Λ-α-[Co(*R*-picpn)Cl_2]$^+$ and (–·–) Δ-β-[Co(*R*-picpn)-Cl_2]$^+$ in concentrated hydrochloric acid at 298 K. Data for the Λ-α-dichloro complex are taken from ref. [1].

the fact that the two H(6) signals of the pyridine rings are observed to be well separated. This is precisely the pattern expected [1] for a β-isomer, (*I*), in which different electronic shielding effects would be felt by these protons.



(*I*)



(*II*)

The circular dichroism spectrum of the β-diastereoisomer is shown in Fig. 1. Two bands of opposite sign are evident in the visible region of the spectrum, the negative one being of lower energy. Comparison of the CD spectrum with those of Λ-[Co(en)$_2$-$(NO_2)_2$]$^+$, Δ-β- and Λ-α-[Co(3*S*,8*S*-dimetrien)-$(NO_2)_2$]$^+$ and Λ-β-[Co(5*R*-metrien)$(NO_2)_2$]$^+$, [18, 19], all of whose absolute configurations have been established crystallographically [20–23], permit us to assign the absolute configuration of the β-isomer as Δ. Spectral details are given in Table II.

The CD spectra of solutions of the material isolated initially showed a mixture of isomers to be present. Dissolution of this material in warm water, followed by cooling the solution in ice, yielded a small amount of solid product (0.13 g). Evaporation of the supernatant gave pure Δ-β-[Co(*R*-picpn)-$(NO_2)_2$]ClO_4. The first material to crystallize was considerably more insoluble in aqueous solution than the Δ-β perchlorate salt. Its electronic and CD spectral data are given also in Table II.

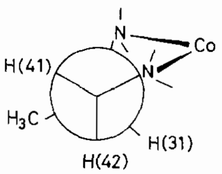
The visible region of the CD spectrum is dominated by a single band of positive sign. Indeed, it is the same species as that isolated by Bosnich [13] and the CD spectrum is enantiomorphic to that reported by Cragel and Brubaker [14] for the [Co(*S*-picpn)-$(NO_2)_2$]$^+$ species. Using the same spectroscopic guidelines outlined above, the absolute configuration of the minor isomer is seen as Λ, and with α-topology.

Analogous solubility differences between α and β isomers of [Co(2*S*,9*S*-dimetrien)$(NO_2)_2$]$^+$ and [Co-(3*S*,8*S*-dimetrien)$(NO_2)_2$]$^+$ have been found [18]. The overall ratio of Δ-β: Λ-α diastereoisomers (inversion: retention) in the isolated fractions is calculated to be 8.4:1.

We are able to show that the inverted product, Δ-β-[Co(*R*-picpn)(NO_2)]$^+$, is thermodynamically more stable in aqueous solution or when dissolved in d_6-DMSO. Rapid isomerization in d_6-DMSO of the Λ-α-diastereoisomer to the Δ-β form prevented the recording of its nmr spectrum in this solvent. Its low solubility in D_2O, and the same isomerization process, prohibited the use of this solvent. However, the interconversion is sufficiently retarded as to allow the measurement of its electronic and chiroptical properties in aqueous solution. This isomerization process was found to be greatly accelerated by exposure of solutions of the Λ-α-isomer to light, with the CD spectrum changing initially to that of the Δ-β-species, and then, with prolonged irradiation by sunlight, to that of an unidentified decomposition product.

These isomerization and subsequent photodecomposition reactions may be contrasted with the behaviour [24] of [Co(en)$_2$$(NO_2)_2$]$^+$. For this latter complex, no such changes were observed. We find that synthesis of the dinitro complex in the dark yields a greater proportion of the Λ-α-diastereoisomer in the solid product. Its isolation here and by other workers [13, 14] would appear to be solely a result of its being the least-soluble diastereoisomer in a mixture of products. Recrystallization from water converts it to the Δ-β isomer almost quantitatively.

The conversion of Λ-α-[Co(*R*-picpn)Cl_2]$^+$ to Δ-β-[Co(*R*-picpn)$(NO_2)_2$]$^+$ is stereospecific in that only one of four possible isomers is obtained. In the Λ-α-isomer both nitrogen N(2) and N(3) atoms are constrained for steric reasons to adopt the *S* configuration. In β-topology, the nitrogen atom not in the fold of the tetradentate may coordinate in either the *R* or *S* configuration. Both kinds of diastereomers have been observed in complexes of trien and its analogues [25]. However molecular models of complexes containing the picpn ligand indicate that considerable strain is imposed on the (N)*R*,(N)*S*-β-isomers. For the (N)*S*,(N)*S*-β- species, there are two possibilities, as shown in (*I*) and (*II*). Analysis of the coupling constants and chemical shifts of the protons in the 1,2-diaminopropane fragment of the tetradentate *R*-picpn ligand permits us to distinguish between these two forms. Each could be viewed as being formed by the edge displacement of opposite pyridyl rings during the substitution. The coupling constants $J_{31,41}$ and $J_{31,42}$ (Table I) are in accord with the Karplus relationship for *quasi-trans* and *gauche* protons on the adjacent carbon atoms of the central ring (*III*), and applied to both of the isomers (*I*) and (*II*). However in isomer (*I*), the hydrogen atom H(41), *trans* with respect to H(31) is shielded by a pyridyl ring. This is also the case in the α-configuration, but not in isomer (*II*). There is a considerable down-field shift in the position of the hydrogen resonance of H(41) with respect to its position in the starting material Λ-α-[Co(*R*-picpn)Cl_2]$^+$, [1]. Thus it would appear that the Δ-β-diastereomer depicted in (*II*) is the one that is formed stereospecifically during the reaction. This isomer has minimal nonbonded interactions between the methyl group and a bridging CH_2 group of the *R*-picpn ligand. Preferential formation of isomer (*II*) may thus simply be due to steric requirements. It was originally pointed out by Bosnich [13] that Λ-α-[Co(*R*-picpn)Cl_2]$^+$ is the isomer of that complex which involves least strain in the coordination sphere. This conclusion was borne out in a strain-energy calculation [26] of several of the possible isomers. While undoubtedly true, this is not to say that the Λ-α-complex should be the thermodynamically most stable one. We have found [1] that it is the least soluble (as the perchlorate salt) of the dichloro diastereomers, but others may be isolated. Both Λ-α- and Δ-α-[Cr(*S*-picpn)Cl_2]ClO_4 have been synthesized, the latter being the more insoluble, and these complexes are isomorphous with their corresponding Co(III) salts [27, 28].



(*III*)

When Δ-β-[Co(*R*-picpn)$(NO_2)_2$]ClO_4 is dissolved in concentrated hydrochloric acid and evaporated to dryness at steam bath temperature, it is quantitatively converted to a dichloro isomer. Its CD spectrum is shown in Fig. 1 and it is seen to be *quasi*-enantiomeric to that of Λ-α-[Co(*R*-picpn)Cl_2]ClO_4, [1]. Thus, its absolute configuration is Δ. However, its 360 MHz ^1H nmr spectrum, recorded in d_6-DMSO (Table I) shows clearly that this species is also a Δ-β-diastereoisomer. It is worth noting that it is much more reddish in the solid state than the α-species. Spectral details are given in Table II.

The reaction to form Δ-β-[Co(*R*-picpn)Cl_2]ClO_4·$2H_2O$ from Δ-β-[Co(*R*-picpn)$(NO_2)_2$]ClO_4 is also stereospecific in that, again, only one of four possible diastereoisomers is obtained, although the conversion may take place with retention or a double inversion of configuration. Inspection of the chemical shifts found for the Δ-β-dichloro isomer indicates that probably it too is that isomer based on (*II*).

We are continuing our studies on the chiral discriminations responsible for such inversions as outlined above and reported previously [1] in this and related systems and will report our findings in subsequent communications.

Acknowledgements

We wish to thank the SERC for a research grant under which some of this work was carried out. One of us (J.A.C.) also thanks the SERC for the award of a studentship.

References

1 J. A. Chambers, T. J. Goodwin, M. W. Mulqi, P. A. Williams and R. S. Vagg, *Inorg. Chim. Acta*, in press.
2 R.C Job, *J. Am. Chem. Soc.*, *100*, 5089 (1978).
3 D. A. Buckingham, I. E. Maxwell, A. M. Sargeson and M. R. Snow, *J. Am. Chem. Soc.*, *92*, 3617 (1970).
4 R. G. Asperger and C. F. Liu, *J. Am. Chem. Soc.*, *89*, 1533 (1967).
5 R. C. Job and T. C. Bruice, *J. Am. Chem. Soc.*, *96*, 809 (1974).
6 J. P. Glusker, H. L. Carrel, R. Job and T. C. Bruice, *J. Am. Chem. Soc.*, *96*, 5741 (1974).
7 D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2673 (1953).
8 E. Kyuno, L. J. Boucher and J. C. Bailar, *J. am. Chem. Soc.*, *87*, 4485 (1965).
9 E. Kyuno and J. C. Bailar, *J. Am. Chem. Soc.*, *88*, 1120 (1966).
10 R. D. Archer, in S. Kirschner (Ed.), 'Coordination Chemistry', Plenum, New York (1969) p.18.
11 A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, *6*, 787 (1967).
12 M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Japan*, *45*, 806 (1972).
13 B. Bosnich, *Proc. Roy. Soc. Ser.A*, *297*, 88 (1967).
14 J. Cragel and G. R. Brubaker, *Inorg. Chem.*, *11*, 303 (1972).

15 B. Bosnich and W. R. Kneen, *Inorg. Chem.*, *9*, 2191 (1940).

16 R. B. Penland, F. J. Lane and J. V. Quagliano, *J. Am. Chem. Soc.*, *78*, 887 (1956).

17 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York (1970).

18 M. Saburi, T. Sawai and S. Yoshikawa, *Bull. Chem. Soc. Japan*, *45*, 1086 (1972).

19 A. J. McCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

20 M. Ito, F. Marumo and Y. Saito, *Acta Cryst.*, *B26*, 1408 (1970).

21 M. Ito, F. Marumo and Y. Saito, *Acta Cryst.*, *B28*, 457 (1972).

22 K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Japan*, *45*, 1755 (1972).

23 K. Tanaka, F. Marumo and Y. Saito, *Acta Cryst.*, *B29*, 733 (1973).

24 S. T. Spees and A. W. Adamson, *Inorg. Chem.*, *1*, 531 (1962).

25 Y. Saito, 'Inorganic Molecular Dissymmetry', Springer-Verlag, Berlin (1979), and refs. therein.

26 G. R. Brubaker and R. A. Euler, *Inorg. Chem.*, *11*, 2357 (1972).

27 Y. Yamamoto and Y. Shimura, *Bull. Chem. Soc. Japan*, *53*, 395 (1980).

28 Y. Hata, Y. Yamamoto and Y. Shimura, *Bull. Chem. Soc. Japan*, *54*, 1255 (1981).