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Cobalt(III) Complexes with Racemic Polyamine Ligands. 1. Isomers Formed Using 5,5,7(*R*,*S*),12,12,14(*R*,*S*)-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet*b*)

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Abstract

cis-[Co(ox)(tet*b*)]ClO_4 is readily isolated from the reaction between tet*b* (tet*b* = *rac*-Me_6-cyclam = 5,5,7(*R*,*S*),12,12,14(*R*,*S*)-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and $K_3Co(ox)_3 \cdot 3H_2O$ in aqueous solution. Removal of the coordinated oxalato ligand by acid hydrolysis (with $HCl/HClO_4$) results in the formation of α-*trans*-(*RRRR*,*SSSS*)-[$CoCl_2${(SSeq,*RR*eq)-tet*b*}]ClO_4 with both six-membered rings in the twist conformation. The (*RR*)-(+)-tartrate (−2) ion coordinates enantioselectively with this isomer to give (−)-*cis*-[Co_2{μ-(*RR*)-(+)-(tart)}{(*RR*)-tet*b*}$_2$]$(ClO_4)_2$ and this, in turn, reacts with $HCl/HClO_4$ to give (−)-α-*trans*-(1*S*,4*S*,8*S*,11*S*)-[$CoCl_2${7*R*eq,14*R*eq)-tet*b*}]ClO_4. The absolute configuration of the tetraamine obtained in the resolution procedure was established by synthesizing the α-*trans*-dichloro isomer using tet*b* of known absolute configuration.

Introduction

meso(tet*a*)** and *racemic*(tet*b*) [5,5,7,12,14-Me_6-cyclam] (Fig. 1) are prepared by reduction of the macrocyclic Schiff base formed by condensation of acetone and singly protonated ethylenediamine [1]. These macrocyclic tetraamines are sufficiently different in their metal ion complex behaviour [2], that they can almost be considered as independent ligands, rather than isomers.

The Ni(II) complexes of tet*b* have been extensively investigated and several *sec*-NH proton isomers of the enantiomeric square planar complexes Ni(*SS*)-tetb^{2+} and Ni(*RR*)-tetb^{2+} have been reported [3, 4]. Removal of the Ni^{2+} (e.g. with CN^-) allows the isolation of the chiral free bases [3].

Although Co(III) complexes of *R*,*S*-tet*a* and *RR*,*SS*-tet*b* were reported in the early days of macrocyclic chemistry [5–9] there has been little recent investigation of the potentially rich stereochemical diversity that is possible using this metal center and these ligands. Work on the octahedral Cr(III) complexes [10–16] of tet*a* and tet*b* shows that *trans* forms predominate for the former and *cis* for the latter. We will show that this generalisation is not as rigid when Co(III) is the metal center.

A complete isomeric enumeration [7, 17] involving axial (ax) or equatorial (eq) C7 and C14 methyl groups, as well as *sec*-NH proton orientations, in *cis* (folded) and *trans* (planar) geometries, indicates that 10 isomers are possible for planar Ni{(*SS*)-tet*b*}$^{2+}$ and 2 isomers for octahedral *cis*-Ni(ox){(*SS*)-tet*b*}. At least 4 square planar Ni{(*RR*,*SS*)-tet*b*}$^{2+}$ isomers are known [17], and of the

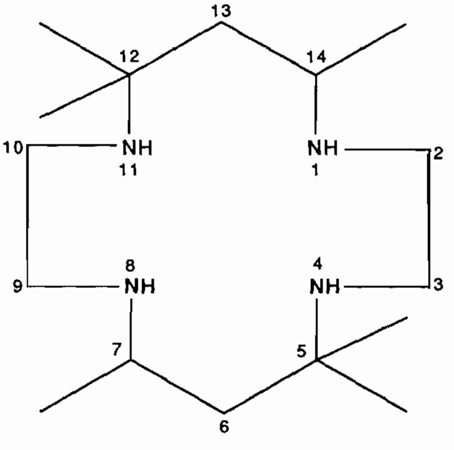

Fig. 1. 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane. The *racemic*-7(*R*,*S*),14(*R*,*S*) isomer is tet*b* and the *meso*-7(*R*),14(*S*) isomer is tet*a*.

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**Abbreviations used: tet*a* = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; tet*b* = *racemic* isomer; ox = $C_2O_4^{2-}$; ACN = acetonitrile = CH_3CN; HTSA = *p*-toluenesulphonic acid; CD = circular dichroism; ORD = optical rotatory dispersion; tart = tartrate (−2) anion.

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six-coordinate folded *cis*-tet*b* metal ion complexes, all known structures [3, 4, 7, 18–23] have the fold axis across the N atoms adjacent to the *gem*-dimethyl groups (*i.e.* the N4, N11 axis, Fig. 1). Such systems result from an approach of the folding bidentate ligand from the less sterically hindered side of the planar α*-(twist,twist)-(*RRRR,SSSS*)-(*SS*eq,*RR*eq)-tet*b* metal isomer.

In this work we describe a direct synthesis of *cis*-[Co(ox)(tet*b*)]ClO_4 and conversion of this by acid hydrolysis to *α-trans*-(*RRRR,SSSS*)-$CoCl_2${*SS*eq, *RR*eq)-tet*b*}]ClO_4. The (*RR*)-(+)-tartrate(−2) ion coordinates enantioselectively [24] when reacted with this isomer, and removal of the tartrate by acid hydrolysis (HCl) produces (−)-*α-trans*-(1*S*,4*S*, 8*S*,11*S*)-[$CoCl_2${(7*R*eq,14*R*eq)-tet*b*}]ClO_4.

Experimental

Racemic tet*b* H_2O was prepared by the method of Hay *et al.* [1] and the (*RR*) and (*SS*) forms using the method of Ito *et al.* [3]. In the following section all complexes were washed successively with 2-propanol and ether and air dried. **Caution**: perchlorate salts are potentially explosive.

Oxalato(tetb)cobalt(III) Perchlorate

$K_3Co(ox)_3 \cdot 3H_2O$ [25] (10 g) dissolved in a minimum amount of water was added dropwise to a hot stirred solution of tet*b*·H_2O (5 g) in a 1:1 MeOH:H_2O solution (200 ml). The solution turned purple and a purple solid deposited. Gentle heating was continued until all the MeOH had evaporated, the solution was cooled and the purple solid removed by filtration. The still purple mother liquor was warmed to 60 °C and $NaClO_4$ (10 g) was added. Purple micro crystals of *cis*-[Co(ox)(tet*b*)]ClO_4 rapidly deposited from the hot solution which was filtered at 60 °C to avoid $KClO_4$ contamination. The original purple solid was dissolved in hot water, filtered if necessary, and $NaClO_4$ added to the hot solution. Deposition of *cis*-[Co(ox)(tet*b*)]ClO_4 was almost quantitative and a total yield of 8 g (88%) was obtained.

This synthesis was repeated on a 1/100 scale using 80% optically pure *RR*-tet*b* [3] to give (−)-(*SSSS*)-Δ_6-[Co(ox){(*RR*)-tet*b*}]ClO_4. CD (H_2O) λ (sign of rotation): 585(+) 560(0), 525(−), 450(0), 380(+) nm.

α-trans-Dichloro(tetb)cobalt(III) Perchlorate

The racemic oxalato perchlorate salt (5 g) was refluxed in aqueous HCl (150 ml, 6 M) until a dark green solution was obtained (~30 min). $HClO_4$ (20 ml, 60%) was added to the still warm solution and green needle crystals (5 g, 95%) deposited from the cooled solution. ^{13}C NMR (ACN) 19.463, 26.034, 31.080, 47.894, 48.882, 52.413, 52.779, 58.204 ppm. ^1H NMR (ACN) 1.325(6H); 1.442(6H); 1.583(3H), 1.604(3H). Visible absorption (ACN) λ (nm), [ε (M^{-1} cm^{-1})]: 658 max [50.8]; 540 min [4.4]; 469 sh [35.2]. IR bands (KBr disc); the band pattern (cm^{-1}) of 770(s), 820(s), 870(m), 900(s), ~980 doublet(m) is characteristic of this isomer.

(−)-μ{(RR)-tartrato}bis{(RR)-tetb}dicobalt(III) Perchlorate Trihydrate

α-trans-[$CoCl_2$(tet*b*)]ClO_4 (0.7 g) and Na[(+)-(*RR*-tartrate] (0.7 g) were dissolved in water (25 ml) at room temperature and 1 M NaOH was added dropwise to pH = 9. The mixture was warmed to 50 °C and $NaClO_4$ (2 g) was added. Three *ca.* 0.05 g crops of the purple crystalline solid were collected after 12 h, 2 days and one week, respectively, retaining the mother liquor. The combined crops were dissolved in 200 ml of 80 °C water and the analytically pure product was precipitated by addition of $NaClO_4$. *Anal.* Calc. for [Co_2(tart)(tet*b*)$_2$]-$(ClO_4)_2 \cdot 3H_2O$: C, 39.75; H, 7.54; N, 10.30. Found: C, 39.25; H, 7.51; N, 10.88%. Visible absorption (1 M HNO_3); λ (nm), [ε (M^{-1} cm^{-1})]: 554 max [500], 384 max [489].

(−)-α-(SSSS)-trans-Dichloro{(7Req,14Req)-tetb} cobalt(III) Perchlorate and its Enantiomer

The above μ-tartrato complex (0.1 g) was dissolved in 5 ml of 6 M HCl at room temperature. After 2 h, 2 ml of 60% $HClO_4$ was added. Green crystals (0.2 g, IR identical with the racemate) deposited overnight. CD(ACN); λ (nm), [Δε (M^{-1} cm^{-1})]: 685(−1.43], 610[+3.85], 530[0], 475-[−2.27], 437(0), 405[+3.15], 365[0]. ORD(ACN); λ (nm), [10^{-3} M, deg M^{-1} m^{-1}]: 642(+3.49], 602[0], 589[−1.11], 565[−1.94], 515sh[−1.60], 478[0], 428[+3.15], 400[0], 380[−1.40], 360-[−1.07]. The (+)-*α*-(*RRRR*)-*trans*-[$CoCl_2${(7*S*eq, 14Seq)-tet*b*}]ClO_4 was isolated by adding 25 ml of 12 M HCl and 5 ml of 60% $HClO_4$ to the above mother liquor from the preparation of the tartrato complex. Green crystals (0.3 g) deposited overnight. The CD and ORD spectra (ACN) were enantiomeric with respect to the data for the (−)-(*SSSS*) isomer.

Results and Discussion

Synthesis and Stereochemistry

Whimp and Curtis [5, 6] prepared *trans*-$CoCl_2$-(tet*b*)$^+$ salts by H_2O_2 oxidation of Co(II)/tet*b* mixtures, but yields were not reported, and using the standard 'air oxidation' method, Chau and Poon [9]

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*This designation conforms with the trivial nomenclature adopted for the Ni^{2+} isomers [3, 17].

report a 36% yield of isolated *trans*-[$CoCl_2$(tet*b*)]-NO_3. We prefer to avoid the use of H_2O_2 or O_2 as oxidising agents as we suspect side chain methyl group oxidation to be a possible reaction [26]. In a search for alternative synthetic routes, we have explored the use of preformed Co(III) complexes as a source of Co(III). Yields of $Co(NO_2)_2$(tet*b*)$^+$ from unbuffered tet*b* plus $Na_3Co(NO_2)_6$ mixtures were not satisfactory, but both $Na_3Co(CO_3)_3 \cdot 3H_2O$ [5, 27] and $K_3Co(ox)_3 \cdot 3H_2O$ [25] give good yields of Co(AA)(tet*b*)$^+$ (AA = CO_3^{2-}, ox^{2-}, respectively) with the oxalato route being the more convenient.

Our discovery that $K_3Co(ox)_3 \cdot 3H_2O$ reacts readily with tet*b*, but not with tet*a*, allows the use of tet*b* that is not entirely free from tet*a* and allows a route to Co(III) tet*b* complexes without necessity of using a highly purified ligand sample or oxidising conditions.

In [Co(ox)(tet*b*)]ClO_4, the ligand has a folded configuration and two *cis* isomers are possible. X-ray structures of *cis*-Cr(AA)(tet*b*)$^+$ (AA = CO_3^{2-}, 2OH$^-$) [11] or *cis*-Ni_2{(*RR*)-tart}{(*SS*)-tet*b*}$_2$(OH_2) [3] show the *RRRR,SSSSsec*-NH configuration is adopted [(*SSSS*) for the chiral Ni(II) complex] and the fold axis is across the N4, N11 axis of the macrocycle (Fig. 2). We will assume a similar configuration for [Co(ox)(tet*b*)]ClO_4, although only the *sec*-NH proton configuration is important in the following argument, as both *cis* isomers will unfold to the same *trans* form once the oxalate is removed.

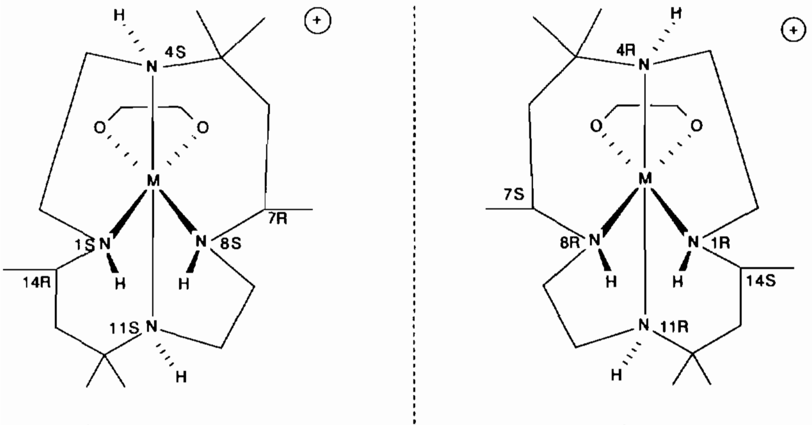
Despite reports to the contrary [6], the oxalate ligand can be removed from [Co(ox)(tet*b*)]ClO_4 with HCl and satisfactory yields of *trans*-[$CoCl_2$-(tet*b*)]ClO_4 can be obtained. This isomer is assumed to have the α-(*RRRR,SSSS*)-(*SS*eq,*RR*eq)-tet*b* configuration with both six-membered rings in the twist conformation (isomer [9] of the Curtis enumeration [7]) as the *sec*-NH proton positions should be maintained in the acid hydrolysis conditions. The ^1H and ^{13}C NMR spectra of this isomer are fully consistent with this assignment.

Removal of the oxalate from [Co(ox)(tet*b*)]-ClO_4 under basic conditions, followed by HCl anation, or recrystallisation of α-[$CoCl_2$(tet*b*)]ClO_4 using the base hydrolysis method of Whimp and Curtis [5], results in a mixture containing at least three other isomeric forms of *trans*-[$CoCl_2$(tet*b*)]-ClO_4. Work is still in progress on the separation and characterisation of these isomers.

The α-[$CoCl_2${(*RR,SS*)-tet*b*}]ClO_4 isomer reacts enantioselectively with Na_2[(*RR*)-(+)-tartrate] to give (−)-[Co_2{(*RR*)-(+)-tart}{(*RR*)-tet*b*}$_2$](ClO_4)$_2$ (evidence for the (*RR*)-tet*b* assignment will be presented later) as the only crystalline product and a Co(III) complex with the coordinated enantiomeric tet*b* ligand remains in solution. Removal of the tartrate from the dinuclear complex with HCl/$HClO_4$ results in the isolation of (−)-α-*trans*-[$CoCl_2$(tet*b*)]ClO_4 and anation of the mother liquor from the resolution procedure with HCl/$HClO_4$ yields the enantiomeric isomer (+)-α-*trans*-[$CoCl_2$-(tet*b*)]ClO_4.

From this sequence alone, it would be difficult to establish the absolute configuration of the resolved diamine. Procedures have, however, been described to obtain both (*RR*)-tet*b* and (*SS*)-tet*b* via resolution of the α-Ni(II) complex and the absolute configuration of (−)-(1*R*,4*R*,8*R*,11*R*)-Ni_2{μ-(*RR*)-(+)-tart-*0,0,0*}{(7*S*,14*S*)-tet*b*}$_2$(H_2O)](ClO_4)$_2$· $2H_2O$ has been established by single crystal X-ray structural analysis [3].

Partially resolved (*RR*)- and (*SS*)-tet*b* were obtained following the method of Ito *et al.* [3] and



Λ5 , Δ6

(1S, 4S, 8S, 11S) - (7Req, 14Req)

Λ6 , Δ5

(1R, 4R, 8R, 11R) - (7Seq, 14Seq)

Fig. 2. Enantiomeric *cis*-M(ox)(tet*b*)$^+$ complexes with the N4, N11 fold axis. Note that the *R* and *S* assignments for the *sec*-NH protons are reversed from those in an identical topology in *cis*-cyclam complexes, due to the methyl substituents on the six-membered rings changing the priority order of the groups attached to the N atom.

the synthetic sequence tet*b* $\rightarrow$ Co(ox)(tet*b*)$^+$ $\rightarrow$ α-*trans*-[CoCl$_2$(tet*b*)]ClO$_4$ was repeated with both chiral forms of the ligand. The use of (*RR*)-tet*b* results in the formation of the (–)-α-*trans*-dichloro and (*SS*)-tet*b* the enantiomeric (+)-α-isomer. Thus the (–) isomer is assigned as (–)-α-*trans*-(1*S*,4*S*,8*S*,11*S*)-[CoCl$_2${(7*R*eq,14*R*eq)-tet*b*}]ClO$_4$ with the *sec*-NH proton assignment following from the absolute configuration of the tetraamine [7].

Two chiral *cis*-complexes have been described here, *viz,* (–)-(1*S*,4*S*,8*S*,11*S*)-[Co$_2${(*RR*)-(+)-tart}-{(7*R*eq,14*R*eq)-tet*b*}$_2$](ClO$_4$)$_2$ and (–)-(1*S*,4*S*,8*S*,11*S*)-[Co(ox){(7*R*eq,14*R*eq)-tet*b*}]ClO$_4$. Comparison of the CD spectra of these (–) complexes with oxalato complexes of known (Δ) absolute configuration leads to the Δ assignment. However, in a macrocyclic ligand of this type, Δ and Λ are ambiguous. Thus, in Fig. 2 the left hand enantiomer could be either Λ_5 or Δ_6 and the resultant CD will depend on which ring pair (5-membered or 6-membered) dominates [28]. In this particular instance we are in a position to decide the issue as the (1*S*,4*S*,8*S*,11*S*)-*sec*NH configuration fixes the six-membered rings in the Δ configuration, independent of the fold axis.

Obviously, the factors that determine which ring pair will dominate are subtle. Previous investigations using (–)-(*RRRR*)-*cis*-CrCl$_2$(cyclam)$^+$ (see Fig. 2 caption) or (–)-(*RRRR*)-*cis*-Cr(NCS)$_2${(*SS*)-tet*b*}$^+$ indicate that the ring pair dominance order may change with the anionic ligand [28] or even the solvent [16]. More information on the CD spectral parameters and absolute configurations for other *cis*-M(X)$_2$(tet)$^{n+}$ (tet = cyclam, tet*a*, tet*b*) complexes is required before generalisations can be made.

Reaction Rates

As described previously, the coordinated oxalate or tartrate ligands can be removed from the *cis* complexes by acid (HCl) hydrolysis, to give α-*trans*-CoCl$_2$(tet*b*)$^+$. The oxalato complex requires hot, concentrated HCl for the reaction to proceed at a measurable rate, but removal of the tartrate is much more facile. Preliminary results show that the tartrate removal process is both H$^+$ and anion dependent and has a half-life of about 16 min at 25 °C in 1 M HCl to give (–)-α-*trans*-(*SSSS*)-CoCl$_2$-{(*RR*)-tet*b*}$^+$. The rate of loss of tartrate with other acids ([H$^+$] = 1 M, 25 °C) is much slower and in the order $H_2SO_4 > HNO_3 >$ *p*-toluenesulphonic acid (HTSA), with less well defined products.

Preliminary data have also been obtained for the rate of loss of chloride ion from α-CoCl$_2$(tet*b*)$^+$ in aqueous acidic media. In 0.1 M HTSA, the reaction proceeds in two steps, corresponding to the loss of one, and then two, chloride ions. The first step [$10^4 \times k_H$ (283 K) = 5.41 s^{-1}] proceeds with apparent retention of configuration, but the second [$10^4 \times k_H$ (298 K) = 8.60 s^{-1}, E_a = 109 ± 2 kJ mol^{-1}, $\Delta S^{\#}$ 54 ± 4 JK^{-1} mol^{-1}] results in a *cis*/*trans*-diaqua mixture. This is entirely consistent with the fact that the two coordinated chloro ligands are not in equivalent positions in this particular isomer.

Previous attempts [8, 9] to measure the rates of acid hydrolysis of *trans*-CoCl(tet*a*)$^+$ or *trans*-CoCl-(tet*b*)$^+$ have resulted in inconsistencies which almost certainly arise from the use of isomerically impure mixtures.

Conclusions

One interesting aspect of this research is the observation that α-*trans*-CoCl$_2${(*RR*,*SS*)-tet*b*}$^+$ reacts enantioselectively with (*RR*)-(+)-tartrate to give (–)-[Co$_2${(*RR*)-tart-*0,0,0,0*}{(*RR*)-tet*b*}$_2$](ClO$_4$)$_2$·3H$_2$O* while α-Ni{(*RR*,*SS*)-tet*b*}$^{2+}$ gives (–)-[Ni$_2$-{(*RR*)-tart-*0,0,0*}{(*SS*)-tet*b*}$_2$(OH$_2$)](ClO$_4$)$_2$ with the opposite ligand enantiomer. Any number of factors could be proposed to account for this difference, but there is probably no more reason to expect similarity than there is to expect that (*RR*)-(+)-tartrate will always form less-soluble salts with the same enantiomer from a series of racemic mixtures [29].

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*We cannot, at this stage, eliminate a formulation for the dinuclear Co(III) complex that corresponds stoichiometrically with the analogous Ni(II) complex.

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