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Article

Alfred Werner's Inorganic Counterparts of Racemic and Mesomeric Tartaric Acid: A Milestone Revisited

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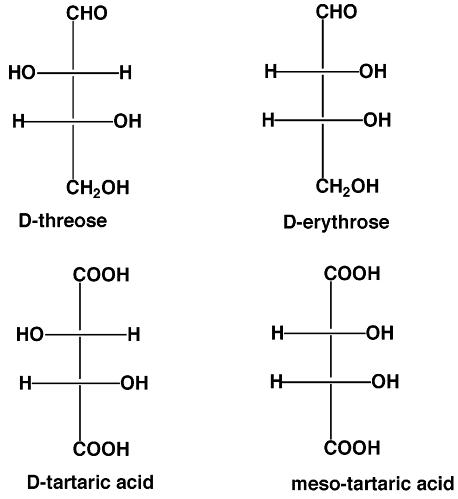
Both isomers of $[(en)_2Co(\mu\text{-}NO_2)(\mu\text{-}NH_2)Co(en)_2]^{4+}$ synthesized by Alfred Werner in 1913 have been optically resolved and are therefore the classic inorganic analogues of the sugars threose and erythrose, rather than the *rac*- and *meso*-tartaric acids, as Werner believed. The nitro bridge is unsymmetrically N–O bonded, and each dinuclear ion is therefore asymmetric, a fact also clearly apparent in the ^1H and ^{13}C NMR spectra.

Introduction

The founder of coordination chemistry, Alfred Werner, was the first to recognize the prospect of the optical resolution of the chiral inorganic complexes *cis*-$[Co(en)_2(NH_3)X]^{2+}$ ($X = Cl^-$ or Br^-), and he, with Victor King, went on to first achieve it.[1] He won the Nobel Prize in Chemistry in 1913 for this and other contributions. He went a monumental step further in the first optical resolution[2] of a completely inorganic species, the famous hexol, $[Co\{Co(NH_3)_4(OH)_2\}_3]^{3+}$, synthesized 16 years earlier[3] by Sophus Mads Jørgensen. Ostensibly, yet another milestone was the synthesis and identification[4] of *meso*- and *rac*-$[(en)_2Co(\mu\text{-}NO_2)(\mu\text{-}NH_2)Co(en)_2]^{4+}$, purported to be the first inorganic analogues of the classic and historically important *meso*- and *rac*-tartaric acids (Figure 1). Werner clearly recognized the potential existence of meso and racemic forms for the bridging amidonitro complex and related species, such as $[(en)_2Co(\mu\text{-}O_2)(\mu\text{-}OH)Co(en)_2]^{4+/3+}$, which bear two identical chiral centers. Indeed, he and others were able to obtain several dibridged complexes in optically active forms,[5,6] but the achiral meso isomers were elusive. They remain so, more than 90 years later.



D-threose

D-erythrose

D-tartaric acid

meso-tartaric acid

Figure 1. Fischer projection diagrams for some classic stereochemical types.

Werner assumed that the nitro group was symmetrically bridged, and that the two chiral Co(III) centers were therefore constitutionally identical. However, several crystal structures[7−12] on nitro-bridged polynuclear Co(III) ions have since revealed the unsymmetrical N−O bridging mode (Figure 2), even the incomplete structural analysis[13] of one form of Werner's $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(en)_2]^{4+}$ ion. IR studies[14−16] support the unsymmetrically bridged NO_2^- formulation. The chiral Co centers in the bridging nitro

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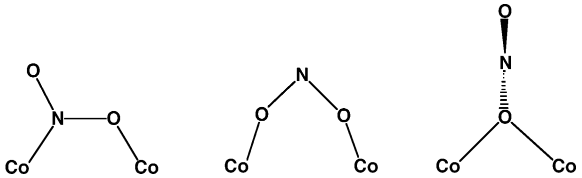

Figure 2. Three possible nitrite ion bridging modes.

complex are therefore dissimilar, and two reviewers[6,17,18] of the works of Alfred Werner have alluded to this.

Since Werner's pioneering work, a rac and meso pair of such dimeric complexes has been synthesized, $[(en)_2Co(\mu\text{-}O_2)(\mu\text{-}OH)Co(en)_2]^{3+}$, for example,[19−21] which are the genuine analogues of *meso*- and *rac*-tartaric acid.

The present study reinvestigates Werner's original $[(en)_2Co(\mu\text{-}NO_2)(\mu\text{-}NH_2)Co(en)_2]^{4+}$ system[4] with the goal of establishing an analogy to the epimeric sugars threose and erythrose through the optical resolution of both isomers.

Results and Discussion

Summary of Werner's Seminal Paper. In 1913, Werner described the synthesis of $[(en)_2Co(\mu\text{-}NO_2)(\mu\text{-}NH_2)Co(en)_2]^{4+}$ and proceeded to crystallize three different bromocamphorsulfonate (BCS) salts.[4] Two of these he ascribed to diastereomeric salts of the D and L forms of the dinuclear complex and the other to a (+)-BCS$^-$ salt of a nonresolvable (meso or anti) form of the complex. One of the three D-BCS$^-$ salts was described as optically inactive (at 589 nm), arising from the fortuitous cancellation of the rotations of the active (−)-dinuclear cation and the four (+)-BCS$^-$ anions. This and other observations on the (+)-BCS$^-$ salts were confirmed by removing the active counteranion and making Br$^-$, I$^-$, and NCS$^-$ salts. He thus obtained three different complex salts, D and L forms exhibiting equal but opposite rotations ($[M] = \pm 1360$ deg M^{-1} dm^2) and an inactive form described as meso. Ostensibly, these results were substantiated by reconstructing a rac salt using the resolved D and L isomers (1:1) and showing that the solubilities of this inactive salt (as the I$^-$) and the inactive meso form were different. The constitutions were also different (Br$^-$, 5 H_2O for rac, 6 H_2O for meso; I$^-$, 0 H_2O for rac, 1 H_2O for meso). Finally, Werner independently made a resolved complex using the resolved (and symmetrical) superoxo ion $[(en)_2Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(en)_2]^{4+}$ by treatment with HNO_2 and HNO_3, and this was identical in all respects to one of the two chiral forms obtained by direct resolution.

Werner went a step further and separately isomerized each of the active forms of the dinuclear complex (as their (+)-BCS$^-$ salts, which are very different in activity and solubility) by boiling in water, and he recovered the products and showed that they were the same material, (+)-BCS$^-$ salts of the inactive complex, identical in solubility and optical activity. Converted to the iodides, they also had the same solubility (but different than the (+)-BCS$^-$ salts) and were optically inactive. These salts were therefore reasonably believed to be those of the meso form.

Werner held this as a strong case for the rac and meso forms of the dinuclear ion (the rac form resolvable and the meso not), and the facts in support of his case, as presented, are hard to dispute. The question of "hauptvalenz" and "nebenvalenz" valences[22] was also deemed to be settled by this work. The ambidentate NO_2^- ligand apparently was attached to the two cobalts either as a symmetrical O−O-bridged or as a single O-bridged ion (Figure 2); a single N-bridged configuration does not seem to be possible. Some have held to a case of O−O bridging,[23] but from what follows, this cannot be true.

In the 90 years since this classic study, the experimental work has never been repeated. The implications for the unsymmetrical bridging of NO_2^- in Werner's *rac*- and supposed *meso*-$[(en)_2Co(\mu\text{-}NO_2)(\mu\text{-}NH_2)Co(en)_2]^{4+}$ complex are now clear. There are just two isomers for the dinuclear ion, but both are asymmetric and potentially resolvable. Another point is that the analogy to the *meso*- and *rac*-tartaric acids disappears, but a new analogy emerges to the threose and erythrose sugars, for example, which are epimeric at one chiral carbon as are the tartaric acids, but which have dissimilar chiral centers (Figure 1).

Repetition of Werner's Work. We have repeated Werner's experiments, with the advantage of ion-exchange chromatography to completely and easily separate the rac (hereafter threo) and meso (erythro) forms and high-field NMR spectroscopy to definitively establish the structures. We have also repeated Werner's solubility measurements to examine the likely prospect that his claimed "unsplittable meso" isomer is our erythro diastereoisomer.

We confirm that there are two forms of the complex, obtained according to Werner's directions, but the ^1H (Supporting Information) and ^{13}C NMR (Figure 3) spectra show quite unambiguously that *both* forms are asymmetric; that is, the nitro bridge is unsymmetrically N−O-bonded, and all ^1H and ^{13}C nuclei are inequivalent. We have also constructed the asymmetric erythro isomer from the new[24] (and genuinely symmetric) *meso*-$[(en)_2Co(\mu\text{-}OH)(\mu\text{-}NH_2)Co(en)_2]^{4+}$ using the same method described for the rac (threo) isomer.

We found the starting material of $[(en)_2Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(en)_2]^{4+}$, synthesized by Werner's original directions,[17,25,26] to be a single isomeric form and known to be the racemic isomer because it has been optically resolved.[26] Its reduced (I$^-$) and diamagnetic peroxo derivative shows a clean four-

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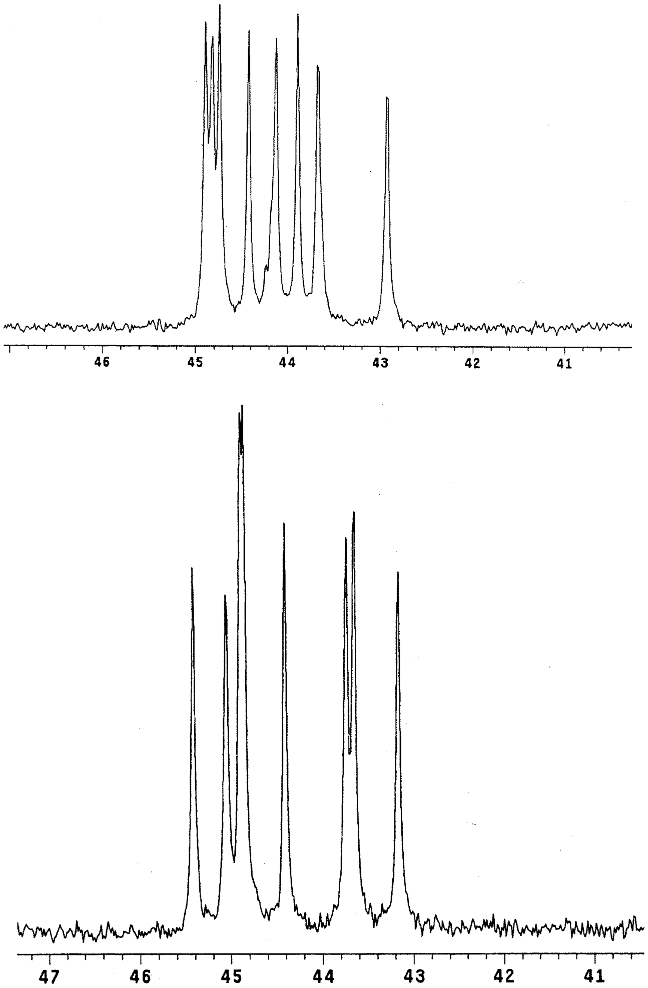

Figure 3. ^{13}C NMR spectra for (top) *threo*- and (bottom) *erythro*-$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(en)_2]^{4+}$ in $Me_2SO\text{-}d_6$.

line ^{13}C NMR spectrum (Figure 4), characteristic of a single isomer that is symmetrically bridged.

Conversion of the bridging peroxo or superoxo ions to the nitro form should therefore result in just the one isomer, and indeed it does. Others[13,23,27] have since synthesized this material, which we relabel as threo.

Given the fact that the nitro bridge is unsymmetrically bonded, both forms of the dinuclear ion are potentially resolvable, and Werner's observations of a resolvable and a nonresolvable form are, in hindsight, curious. Nonetheless, it is now clear that the rac (threo) form, synthesized independently from the superoxo complex or from the tetraammine complex by reaction with en, is the same material. The resolved superoxo complex gave the resolved threo ion. The remaining issue then became the identity and resolvability of the so-called meso (erythro) isomer.

We are forced to the conclusion that Werner did obtain both isomeric forms, but that his "unsplittable meso" form was an unresolved racemate, the rac erythro isomer. There must be two (+)-BCS$^-$ salts for the threo and two (not one) for the erythro isomer (he apparently missed the fourth (+)-BCS$^-$ salt).

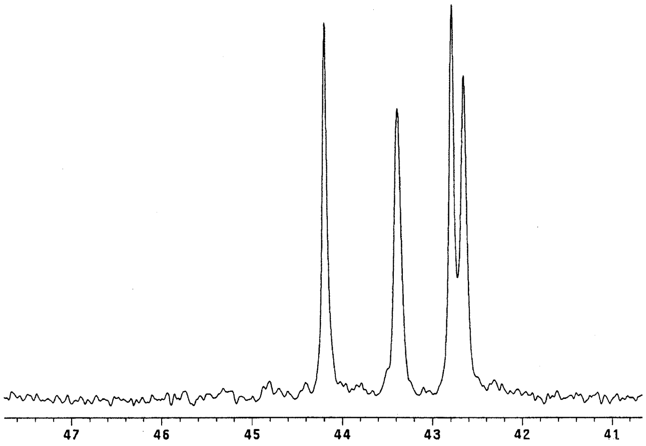

Figure 4. ^{13}C NMR spectrum for *rac*-$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(en)_2]I_3$ in $Me_2SO\text{-}d_6$.

It is interesting to observe the vivid and detailed descriptions of the morphologies of the various salts of the dinuclear species in the original publication of 1913. In particular, Werner described the (+)-BCS$^-$ salt of the meso dinuclear ion of irregular morphology, and later he noted that the crystals of the same salt derived from isomerization of the (+)-BCS$^-$ salt of either the D or L form by prolonged boiling in water were not exactly the same. The solubilities of the salt obtained by any of the three ways were noted as identical, however.

We suspect that Werner obtained his meso isomer as a mixture of two D-BCS$^-$ diastereomers present in nearly equal amounts. He reports a molar rotation for the (+)-BCS$^-$ salt of his meso form of +1285 deg mol^{-1} dm^2. One can calculate from his [M] data for the (+)-BCS$^-$ salts of the D and L complexes (+2828 and, quite accidentally, 0 deg mol^{-1} dm^2, respectively) that the chiral cations for the resolved rac isomer contribute ±1414 deg mol^{-1} dm^2 to [M] and the four (+)-BCS$^-$ anions +1414 deg mol^{-1} dm^2. (The error suggested by the significant figures is almost certainly larger than this. For example, his [M] values for two samples of the Br$^-$ salts of the D complex, the first obtained by direct resolution and the second from a preresolved precursor, are +1360 and +1311 deg mol^{-1} dm^2.) Thus, [M] = +1414 deg mol^{-1} dm^2 is the calculated value for the (+)-BCS$^-$ salt of a genuine meso species. The observed value is +1285 deg mol^{-1} dm^2, a difference to the calculated value of +1414 deg mol^{-1} dm^2 sufficient to suggest Werner's meso species may indeed have been active, even weakly, for the complex ion portion of the (+)-BCS$^-$ salt.

Gillard et al. studied the resolved dinuclear ions extensively, including the present (+)-threo amidonitro species, and deduced the absolute configurations through bridge cleavage reactions and the comparison of ORD and CD spectra for known mononuclear derivatives. Our molar rotations for the D isomer are in close agreement with those gleaned from their ORD curve, and we confirm that the nitro bridge is cleaved with the predominant retention of configuration and optical activity in aqueous OH$^-$. We have carried out a similar reaction on the erythro isomer, which also proceeds with predominant retention (but with a complete

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loss of optical activity), to generate upon reacidification (pH ca. 7) the new *meso*-$[(en)_2Co(\mu\text{-}OH)(\mu\text{-}NH_2)Co(en)_2]^{4+}$ complex. This result confirms the erythro configuration for the starting material.

In an effort to understand Werner's inability to resolve his meso isomer, we suspected the optical activity for the fully resolved erythro ion, an "almost meso" configuration, may have been small due to cancellations from its Λ and Δ components. However, we found this not to be the case, and it seems there is enough wavelength offset in the ORD spectra from the $\Lambda\text{-}CoN_5O$ and $\Delta\text{-}CoN_6$ components to avoid substantial cancellation.

Further questions about Werner's meso isomer have been answered experimentally. By boiling aqueous solutions of the rac form of $[(en)_2Co(\mu\text{-}NO_2)(\mu\text{-}NH_2)Co(en)_2]Br_4$, we have isolated the meso form and characterized it completely. We now know this is not a meso but rather an erythro isomer. Werner reported that his D and L active (+)-BCS^- salts converted to the same meso (+)-BCS^- salt with prolonged boiling. We dispute this. Two different salts must have resulted, but he was unable to differentiate between the two.

Werner also commented on his inability to achieve the same amount of D and L isomers of his rac form of the bridging amidonitro complex. He quite reasonably rationalized this observation as arising from the preferential isomerization of the D isomer of the complex which, because of its decreased solubility in hot water as its (+)-BCS^- salt, had more opportunity (the D isomer was largely undissolved under these conditions, and prolonged boiling was required to dissolve it). By repeating Werner's experiments, but with some modifications, we observed the reverse (more D isomer than L). We limited the boiling time in water, and the excess of D isomer quite clearly arose from the fact that, for our over-resolved racemate, we initially crystallized a mixed (+)-BCS^- salt (containing mostly D but also appreciable L). Thus, not much of the least-soluble D salt was in solution during the subsequent boiling water extraction procedures and, therefore, was left untouched while the more soluble L salt was partly isomerized.

This discussion of isomerization in solution leads to a consideration of why Werner apparently obtained a racemic erythro isomer via this process.[28] The conversion of the threo to the erythro isomer requires inversion of one cobalt center. Inversion at cobalt normally occurs via ligand substitution, but here, there is no good leaving group. Another option is catalysis by Co(II), generated through reduction under the forcing (boiling) conditions. A third prospect is the intramolecular rearrangement about one of the Co(III) centers, a phenomenon not unknown, and for a complex with a single NH_2^- bridge, it might not be unexpected. Whatever the mechanism, the epimerization at one of the two dissimilar chiral Co centers occurs. We observed no detectable Co(II) under the forcing conditions (Co(II) elutes well in front of the 4+ cations on Dowex, and is readily observed through the Kitson test[29]).

An important consideration is whether epimerization at cobalt leads to not only the threo to erythro conversion but also the racemization of both species. The two cobalt centers are different (one has the $(en)_2Co(NH_2)(ON)$ constitution, the other $(en)_2Co(NH_2)(NO)$), and it seems reasonable to assume that one inverts faster than the other. The idea is that the fully resolved rac isomer might first yield one antipode of the erythro isomer by selective inversion at one chiral Co(III) center.

We have tested these prospects experimentally. Several fractions of (+)-BCS^- salts were derived from the original racemate by successive extractions with hot water until no complex remained, as Werner had done. However, we went several steps further through the re-extraction of each of these with hot water and further fractionated the salts, reducing the volume of the filtrates to obtain additional crops. All filtrates were then combined and chromatographed on Dowex to provide additional resolved rac isomer (band 1) and meso (band 2) material, which were separately fractionated as various salts, as well. In all, we obtained some 50 fractions of Cl^-, Br^-, I^-, NO_3^-/ClO_4^-, or $Cl^-/ZnCl_4^{2-}$ double salts. The D- and L-threo fractions arose largely from the (+)-BCS^- salts, whereas most of the meso forms came from the combined filtrates after ion-exchange chromatography. All were examined by UV−vis spectroscopy and polarimetry and by NMR spectroscopy (Supporting Information and Figure 3).

We confirm that Werner's least-soluble (+)-BCS^- salt yields the D series of complexes, and that the most-soluble salt gives the L series. However, our meso fractions all proved to be active (to varying degrees) and all with the same sign (+) of rotation (at any particular wavelength), and thus both enantiomers were present. There was, however, a clear preponderance of one optical isomer, which suggests this was indeed derived from the L-threo form by selective inversion at one of the chiral Co(III) centers, as suggested earlier.

The D enantiomer for the threo isomer exhibits a ++++ pattern for the optical rotations measured in water (589, 578, 546, and 436 nm, respectively), while the erythro isomer shows a +++− pattern. Maximum values obtained for the Br^- salts of the active threo isomers were $[M]_D = +1520$ deg mol^{-1} dm^2, $[M]_{578} = +1587$ deg mol^{-1} dm^2, and $[M]_{436} = +6390$ deg mol^{-1} dm^2 (all + or −), which compare favorably to Werner's $[M]_D = \pm1361$, ±1282, and ±1299 deg mol^{-1} dm^2 for his Br^-, I^-, and NCS^- salts, respectively. With the 4+ cations, small differences can easily arise through ion pairing, which is known to affect ORD and CD spectra in the visible region. For the active erythro, we observed maximally $[M]_{578} = +1818$ deg mol^{-1} dm^2 and $[M]_{436} = -860$ deg mol^{-1} dm^2, but most fractions had values about one-half of these. These compare with Werner's $[M]_D$

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(28) Werner went to some pains to reconstruct a racemic isomer from a 1:1 mixture of the separated D and L forms and to show through solubility measurements that it was different than his inactive meso complex.

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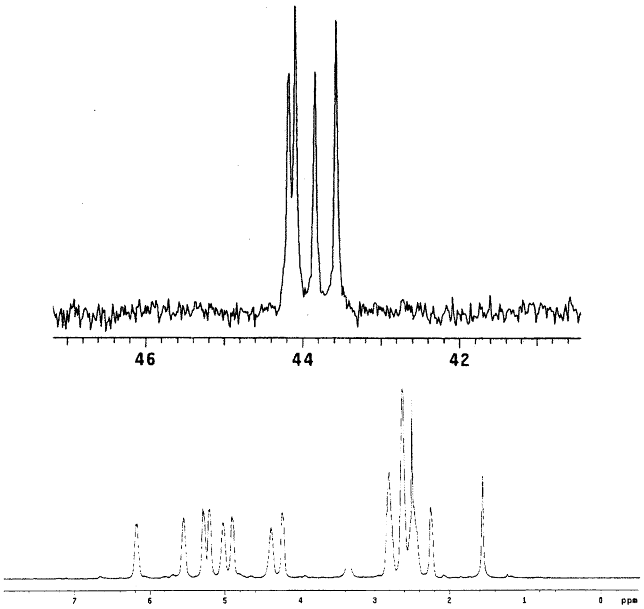

Figure 5. ^{13}C (top) and ^1H NMR (bottom) spectra for the symmetrically bridged dinuclear complex impurity in Me_2SO-d_6; the counterions are $(Cl^-)_2\cdot ZnCl_4^{2-}$.

= 0 deg mol^{-1} dm^2 for his "unsplittable meso", and clearly here lies the key difference between the present and earlier work.

Finally, we measured the solubilities for the iodide salts to compare with Werner's results. For our racemic erythro isomer (meso), we observe a solubility of 1.55 g/100 mL at 21 °C and 1.25 g/100 mL at 19 °C, compared to Werner's value of 2.44 g/100 mL at 19 °C. For our racemic threo salt, we find a solubility of 2.68 g/100 mL at 19 °C, whereas Werner reports 3.75 g/100 mL at 19 °C. Our results are lower than Werner's, and the only agreement is that his meso form is about 2-fold less soluble than the rac form.

The IR spectra are unremarkable, with bands attributable to N$-$O bridging NO_2^-, evident in the KBr disks of the iodide salts at 1493 and 1145 cm^{-1} for the threo isomer and 1491 and 1153 cm^{-1} for the erythro isomer. The IR spectra of the corresponding μ-OH salts were used for assisting in the identification of these bands since an extra-sharp peak (unassigned) appears at about 1526 cm^{-1} in both the hydroxo and nitro complexes. The UV$-$vis spectra for the two isomers are essentially identical, as expected.

Do the Symmetrically Bridged NO_2^- Dinuclear Species Exist? The conversion of the *threo*- to the *erythro*-$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(en)_2]^{4+}$ dinuclear ions in boiling water is accompanied by the formation of a byproduct, which elutes on Dowex with the faster-running threo isomer and is clearly also a 4+ ion. Isolated crystals from this first band show an impurity that has a set of four lines in its ^{13}C NMR spectrum (Figure 5, top), and a simpler ^1H NMR spectrum (8 rather than 16 NH resonances (Figure 5, bottom)) that corresponds to a symmetrically bridged species.

We initially believed this complex to be the elusive O$-$O-bonded nitrite complex because of the color and charge and the fact that it revealed a sharp line at 1054 cm^{-1} in its IR spectrum (KBr disk), suggestive of the O$-$O-bridged NO_2^-. The ^1H NMR spectrum revealed no evidence of the characteristic bridging of OH^- at a high field, eliminating the likely alternative, the known red complex, *rac*-$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2]^{4+}$. Nonetheless, the treatment of *rac*-$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2]^{4+}$ with HCl and the slow crystallization using H_2ZnCl_4 as a precipitant yielded a red-violet complex bearing a dinuclear cation identical to that of the impurity, and analyzing as $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}Cl)Co(en)_2]Cl_2\cdot ZnCl_4\cdot 2H_2O$. It seems that boiling the nitro-bridged ion in HCl leads to a little cleavage of the robust nitro bridge with the elimination of HNO_2.[30] This byproduct therefore contains no NO_2^- at all and is analogous to the known and structurally characterized octaammine species $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}Cl)Co(en)_2]^{4+}$.[31] The ethylenediamine complex is more stable than the octaammine, and the Cl^- bridge is retained in a Me_2SO-d_6 solution. It is the rac isomer; we have also synthesized the meso isomer.[24]

Molecular models of the $[Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co]$ bridge system suggest that N$-$O bridging is more strained than the single-bridged O or dibridged O$-$O structures (Figure 2). However, the Co$-$N-bonded nitro complex, $[Co(NH_3)_5NO_2]^{2+}$, is well-known to be more stable than the Co$-$O nitrito form, $[Co(NH_3)_5ONO]^{2+}$, and the bond strength factor appears to remain dominant in the nitro-bridged dinuclear metal-ion ring systems. Also relevant here are the O- and S-bonded sulfinate and sulfenate metal-ion systems where one can control the S- or O-bonding by constraining the ring, of which the functional group is a part, to being four-, five-, or six-membered.[32−35]

We remain optimistic that a less stable O$-$O-bridged nitrito complex can be synthesized. There are signs that in the related $[(en)_2Co(\mu\text{-}OH)(\mu\text{-}NO_2)Co(en)_2]^{4+}$ system a transient species believed to be a nitrito complex can be crystallized through controlled nitrosation of the precursor bridging peroxo or superoxo complexes, but which leads ultimately to the usual N$-$O dibridging mode.[24]

Experimental Section

All chemicals were AnalaR or an equivalent grade. Silver D-bromocamphorsulfonate was prepared in water from a 1:1 mixture of freshly precipitated silver oxide and ammonium d-bromocamphorsulfonate (Aldrich); the ammonia was removed by rotoevaporation at ca. 40 °C in the absence of light. Carbon-13 and proton NMR spectra were recorded on Varian XL-300 and Unity Plus 400 MHz instruments at 20 °C. Solvents used were D_2O with dioxane as the internal reference (^{13}C, δ 69.27 ppm relative to DSS) and Me_2SO-d_6 with the central peak of the CD_3 septet as the reference (^{13}C, δ 39.37 ppm relative to $SiMe_4$). ^1H NMR spectra reported for Me_2SO-d_6 as the solvent are for perchlorate or nitrate perchlorate salts. UV$-$vis absorption spectra were recorded on a HP8452A

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(30) Although the bridging nitro complex is reported as very unreactive (ref 17), the bridge can be completely cleaved in base, readily, and also in hot triflic acid with heating.

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diode array spectrophotometer. Optical rotations were obtained using a Perkin-Elmer PE241 instrument (25 °C; 1 cm and 1 dm cells). Infrared spectra were recorded as KBr disks on a Bio-Rad FTIR model FTS165 (300−4000 cm^{-1}). The cation exchange medium used was Dowex 50Wx2 (H^+ form, 200−400 mesh; Bio-Rad). Microanalyses were performed in the microanalytical laboratories at the Research School of Chemistry, ANU.

Solubility measurements were performed by stirring an excess of the iodide salts of *rac-threo-* or *erythro-*$[(en)_2Co(\mu\text{-}NO_2)(\mu\text{-}NH_2)Co(en)_2]^{4+}$ (ca. 0.2 g samples) in water (ca. 10 mL) for 30 min at either 19 or 21 °C. The saturated supernatants were decanted and diluted accurately either 3-fold (erythro) or 6-fold (threo) using Pipetmen, and then the visible absorption spectra were recorded. Concentrations were determined using $\epsilon_{476} = 340\ M^{-1}\ cm^{-1}$ for the erythro isomer and $\epsilon_{476} = 335\ M^{-1}\ cm^{-1}$ for the threo form.

Synthesis. The bridging peroxo complex, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{4+}$, was generated in situ, treated with aqueous ammonia and KOH to generate the dibridged μ-amido−μ-peroxo species, and then oxidized in situ with Ce^{4+} to yield the more stable amido−superoxo derivative, which was crystallized as the nitrate salt.[17,36,37] Chlorine gas as an oxidant was as equally effective as Ce(IV). This complex was then reacted with aqueous ethylenediamine as described[17] to yield the $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(en)_2](NO_3)_4$ salt. Reaction[4] with $NaNO_2$ and HNO_3 then afforded the desired $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(en)_2](NO_3)_4$ salt in good yield. An alternative procedure is the reaction of the μ-amido−μ-superoxo tetraammine complex with $NaNO_2/HNO_3$, which yields $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(NH_3)_4](NO_3)_4$, followed by the reaction with aqueous ethylenediamine; the former route is preferred. Yet another method has been described by Garbett and Gillard.[23]

rac- and *meso-*$[(en)_2Co(\mu\text{-}OH)(\mu\text{-}NH_2)Co(en)_2]I_4$ were obtained as described elsewhere.[24,38] A sample of the optically resolved rac isomer[23,26] of the superoxo species, $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(en)_2]^{4+}$, was treated with $NaNO_2/HNO_3$ as described above to yield an authentic specimen of resolved *threo-*$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(en)_2]^{4+}$, isolated as the nitrate salt. This compound can also be synthesized from the bridging peroxo[39] or hydroxo ions by nitrosation; the meso and rac forms for all of these species are now known.[24] Salts of the *meso-*$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2]^{4+}$ complex were treated with $NaNO_2/HNO_3$ as described above for the rac species to provide an alternative synthesis of the *rac-erythro-*$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(en)_2](NO_3)_4$ material.

A sample of the *rac-threo-*$[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(en)_2](NO_3)_4$ complex was boiled in water for 45 min and then diluted and sorbed on a column of Dowex resin. Elution with 3 M HCl resulted in two bands, the first (major) being the starting material and the second (minor) being the erythro isomer. The complexes were recovered by rotoevaporation and crystallization of the residues from a minimum volume of water using 5 M HNO_3 as the precipitant. The experiment was repeated using a pure erythro isomer as the reactant, with a similar result, establishing an equilibrium between the threo and erythro isomers, with the threo being the predominant species. The threo and erythro complexes were isolated as a variety of salts. Threo isomer analysis follows. Anal. Calcd for $[(C_2H_8N_2)_2Co(NH_2)(NO_2)Co(C_2H_8N_2)]I_4{\cdot}0.5NaI{\cdot}0.5H_2O$: C, 9.50; H, 3.49; N, 13.85; I, 56.43. Found: C, 9.50; H, 3.55; N, 13.66; I, 57.31. Erythro isomer analyses follow. Anal. Calcd for $[(C_2H_8N_2)_2Co(NH_2)(NO_2)Co(C_2H_8N_2)]Cl_4{\cdot}6H_2O$: C, 14.34; H, 6.92; N, 20.91; Cl, 21.26. Found: C, 14.69; H, 6.21; N, 20.41; Cl, 21.27. Anal. Calcd for $[(C_2H_8N_2)_2Co(NH_2)(NO_2)Co(C_2H_8N_2)]I_4$: C, 10.16; H, 3.84; N, 14.81; I, 53.66. Found: C, 10.29; H, 3.85; N, 14.53; I, 53.56. Anal. Calcd for $[(C_2H_8N_2)_2Co(NH_2)(NO_2)Co(C_2H_8N_2)](NO_3)_2(ClO_4)_2{\cdot}3.5H_2O$: C, 11.92; H, 5.13; N, 20.85; Cl, 8.79. Found: C, 12.19; H, 4.66; N, 20.89; Cl, 8.58. The threo isomer also crystallized readily as a mixed nitrate−perchlorate salt but did not exhibit a consistent stoichiometry but rather with nonintegral nitrate and perchlorate counterions. Other salts were analyzed for Co spectrophotometrically using the extinction coefficients recorded herein. The threo iodide was obtained as a monohydrate, while the corresponding erythro iodide was anhydrous (microanalysis; ^1H NMR analysis[40] for H_2O in dry $Me_2SO\text{-}d_6$), the reverse of that reported by Werner.

The optical resolution of *threo-*$[(en)_2Co(\mu\text{-}NO_2)(\mu\text{-}NH_2)Co(en)_2]Br_4$ salt was carried out as described by Werner[4] on the same scale and using 4 equiv of Ag(+)-BCS but with minor variations (as noted in the Results and Discussion). The ratios α_{578}/A_{476} and α_{436}/A_{476} were used for monitoring the progress of the resolution and subsequent exhaustive fractionation of the salts derived from the (+)-BCS^- salts and the filtrates recovered from the ion-exchange column; $[M]_\lambda$ values were calculated for each fraction from these data and using the extinction coefficients recorded herein.

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Supporting Information Available: Figure with ^1H NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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