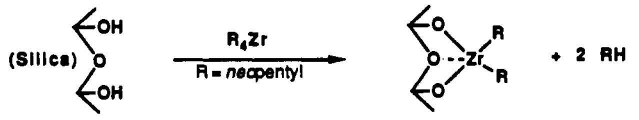

Figure 1. Possible ligation of Zr in (silica)ZrR_2. Note: This implies that two OH groups of the support have reacted on deposition (as determined by measurement of RH evolution); one μ-oxo group is suggested also to be coordinated to Zr resulting in 5-coordinate Zr(IV).

can interact with the metal. In this representation (Figure 1), two oxygen atoms are "doubly" bridged and one is "triply" bridged, and all Zr-O-Si angles are "bent". Electron counting for this arrangement can be done on the basis of structures reported for ZrO_2 (baddeleyite) and for soluble complexes containing Zr-O linkages. Baddeleyite contains two types of oxygen atoms:[28] tetrahedral, quadruply bridging ones ("sp^3") and planar, triply bridging ones ("sp^2"). Two of the three triply bridged Zr-O bonds are significantly shorter (2.05, 2.06 Å) than the five others in the unit cell (2.15-2.28 Å), suggesting π-interactions might exist for these oxygens (by "octet rule" electron counting, a $^1/_2$ π-bond order for each of these short interactions). π-Interactions for doubly Zr-bridging oxygens are also likely for $(Cp_2ZrX)_2O$ species (X = Cl,[29a] CH_3[29b]) and for $(tritox)_2Zr$ systems[14] (tritox = $[(CH_3)_3C]_3CO^-$); in these cases[14,29] nearly linear Zr-O-Zr and C-O-Zr units and short Zr-O bonds (Zr-O = 1.94 and 1.895 Å, respectively) are consistent with sp O and multiple π-interactions per O. With this notion of multiple bonding, $(tritox)_2ZrCl_2$ has been described as a 16e system in which each O of the alkoxide acts as a Cp^- analogue;[14] similarly, (silica)ZrH_2 can be thought of as a 16e species in which each of the three oxygen atoms of the support ligand serves as a 4e donor and (silica)ZrHCl, through Cl to Zr π-donation, as an 18e species.

Acknowledgment. We acknowledge support of this work by the National Science Foundation.

Supplementary Material Available: Infrared spectra of silica-supported zirconium complexes (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Physics
and School of Chemistry and Applied Chemistry,
University of Wales College of Cardiff,
Cardiff CF1 3TB, Wales, U.K., and School of Chemistry,
Macquarie University, Sydney, NSW 2109, Australia

Chiral Metal Complexes. 32.[1] Use of an Optically Active Complex for a Nearly Absolute Chiral Induction

Malcolm A. Anderson,[2] Ewan F. Birse,[3] Michael J. E. Hewlins,[3] John P. G. Richards,[2] Frederick S. Stephens,[4] Robert S. Vagg,*[,4] and Peter A. Williams*[,3]

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It has been shown[5] that ternary, chiral coordination complexes comprising an optically active tetradentate and a substituted aminomalonate ligand (I) may be synthesized in high yield. Considerable discrimination may be obtained with respect to the mode of coordination of the aminomalonate, depending upon the nature of the tetradentate ligand. This may be employed in subtle ways to produce optically active aminoacidates via decarboxylation of the coordinated aminomalonate in aqueous acid.[6]

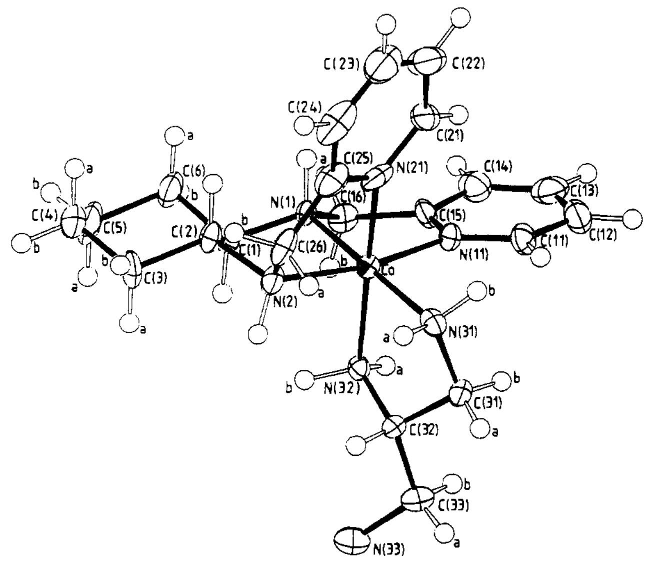
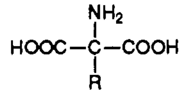
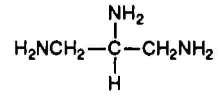


Figure 1. Perspective drawing of the Λ-β_2-[Co(*R*,*R*-picchxn)(tap)]$^{3+}$ cation showing the atomic-labeling scheme. Thermal ellipsoids are scaled to include 35% probability. Hydrogen atoms are labeled according to the atom to which they are bonded for example, that to C(11) is H(11) or that to N(1) is H(N1). Where more than one hydrogen atom is bonded to a given atom they are labeled a and b and for clarity only these labels are included for the hydrogen atoms in the diagram.



$$HOOC-\underset{\displaystyle R}{\overset{\displaystyle NH_2}{C}}-COOH$$

I



$$H_2NCH_2-\underset{\displaystyle H}{\overset{\displaystyle NH_2}{C}}-CH_2NH_2$$

II

Other prochiral branched terdentates could be used to similar effect. Should subsequent reactions be performed that do not involve the newly created chiral center, completely stereospecific chiral inductions are possible. One such prochiral terdentate is Mann's triamine, 1,2,3-triaminopropane (tap, II), which could be used as a precursor for a number of optically active vicinal diamines providing five-membered chelate ring formation is involved. Some 50 years ago, Mann[7] showed that tap could be coordinated to Pt(II) and Pt(IV), with selective formation of five-membered chelate rings, and that $[Pt(tap)Cl_4]\cdot HCl$ and $[Pt(tap)Cl_2]\cdot HCl$ could be resolved into enantiomeric forms.[7] Unfortunately, these resolutions proved to be somewhat tedious, and the optically active complexes racemize in aqueous solution. Other systems may be used to overcome these difficulties, as with the researches of Wild et al.[8] on the stereoselective coordination of glycerol to a chiral Pt(II) complex.

We have examined the coordination behavior of Mann's triamine with a Co(III) complex containing the chiral tetradentate *N*,*N'*-bis(2-picolyl)-(1*R*,2*R*)-diaminocyclohexane (*R*,*R*-picchxn)

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(3) School of Chemistry and Applied Chemistry, University of Wales College of Cardiff.

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Table I. Final Atomic Coordinates (fractional × 10^4) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

	x/a	*y/b*	*z/c*	occ[a]
Co	2479.8 (26)	541.1 (10)	1262.6 (7)	
N(11)	1109 (14)	1402 (6)	1438 (5)	
N(1)	970 (14)	−93 (6)	1643 (5)	
N(2)	3592 (15)	−456 (7)	1206 (5)	
N(21)	3566 (16)	650 (8)	2006 (5)	
N(31)	3981 (14)	1213 (7)	861 (5)	
N(32)	1641 (12)	429 (6)	429 (5)	
N(33)	1359 (20)	328 (9)	−953 (6)	
C(31)	3388 (19)	1486 (8)	277 (6)	
C(32)	2656 (23)	782 (8)	−10 (6)	
C(33)	1934 (21)	1020 (11)	−609 (6)	
C(11)	1398 (19)	2174 (9)	1424 (7)	
C(12)	374 (23)	2745 (10)	1556 (8)	
C(13)	−1020 (23)	2461 (12)	1720 (7)	
C(14)	−1354 (21)	1675 (11)	1748 (8)	
C(15)	−255 (19)	1157 (8)	1579 (6)	
C(16)	−442 (16)	292 (10)	1547 (7)	
C(1)	1083 (21)	−923 (9)	1440 (6)	
C(2)	2755 (15)	−1101 (8)	1526 (7)	
C(3)	3121 (24)	−1926 (9)	1295 (9)	
C(4)	2132 (23)	−2531 (10)	1646 (8)	
C(5)	628 (33)	−2357 (11)	1578 (11)	
C(6)	181 (22)	−1507 (9)	1817 (8)	
C(21)	3263 (21)	1165 (10)	2468 (7)	
C(22)	4182 (31)	1197 (15)	2948 (8)	
C(23)	5449 (32)	737 (15)	2974 (11)	
C(24)	5701 (20)	242 (14)	2519 (11)	
C(25)	4818 (19)	181 (11)	2038 (8)	
C(26)	5005 (19)	−330 (9)	1518 (8)	
Cl(1)	7501 (6)	1450 (3)	217 (2)	
Cl(2)	4775 (5)	3177 (2)	1968 (2)	
Cl(3)	196 (6)	153 (3)	3318 (2)	
O(1a)	7049 (14)	798 (7)	575 (7)	
O(1b)	7005 (18)	1417 (11)	−370 (6)	
O(1c)	9049 (13)	1503 (8)	228 (6)	
O(1d)	6864 (20)	2117 (8)	515 (7)	
O(2a)	6058 (15)	3652 (7)	2043 (5)	
O(2b)	3904 (20)	3166 (9)	2487 (7)	
O(2c)	5152 (19)	2404 (7)	1802 (7)	
O(2d)	3924 (20)	3515 (10)	1518 (9)	
O(3a)	1268 (19)	−307 (10)	3009 (6)	
O(3b)	245 (85)	925 (50)	3118 (59)	0.45
O(3c)	933 (32)	632 (18)	3760 (11)	0.80
O(3d)	−1106 (35)	−252 (33)	3348 (32)	0.50
O(3e)	−333 (61)	−209 (24)	3830 (19)	0.60
O(3f)	−323 (39)	667 (14)	2908 (10)	0.65
O(w1)	2827 (27)	3336 (10)	4635 (5)	
O(w2)	6408 (25)	105 (13)	4342 (10)	0.65
O(w3)	2561 (90)	1080 (21)	4859 (20)	0.45
O(w4)	3991 (63)	1140 (24)	4819 (16)	0.55
O(w5)	263 (73)	964 (24)	5071 (17)	0.35

[a] Occupancy is unity unless otherwise stated.

Table II. Selected Bonding Parameters and Interatomic Distances in Λ-β-[Co(*R*,*R*-picchxn)(tap)]$(ClO_4)_3 \cdot 3H_2O$[a]

(a) Bond Lengths (Å)

Co–N(11)	1.966 (12)	N(31)–C(31)	1.50 (2)
Co–N(1)	1.949 (12)	C(31)–C(32)	1.51 (2)
Co–N(2)	1.979 (12)	C(32)–N(32)	1.48 (2)
Co–N(21)	1.955 (13)	C(32)–C(33)	1.55 (2)
Co–N(31)	2.001 (13)	C(33)–N(33)	1.50 (2)
Co–N(32)	2.036 (11)		

(b) Bond Angles (deg)

N(11)–Co–N(1)	82.5 (5)	N(11)–Co–N(2)	167.6 (5)
N(21)–Co–N(2)	82.8 (6)	N(1)–Co–N(31)	178.2 (5)
N(1)–Co–N(2)	85.5 (5)	N(21)–Co–N(32)	171.6 (5)
N(31)–Co–N(32)	84.1 (5)	N(21)–Co–N(1)	92.1 (5)
N(11)–Co–N(21)	94.7 (5)	N(21)–Co–N(31)	89.0 (5)
N(11)–Co–N(31)	96.1 (5)	N(1)–Co–N(32)	94.9 (5)
N(11)–Co–N(32)	90.8 (5)	N(2)–Co–N(31)	96.0 (5)
Co–N(31)–C(31)	109 (1)	N(2)–Co–N(32)	93.2 (5)
Co–N(32)–C(32)	110 (1)	N(32)–C(32)–C(31)	108 (1)
N(33)–C(33)–C(32)	113 (1)	N(32)–C(32)–C(33)	115 (2)
N(31)–C(31)–C(32)	107 (1)	C(31)–C(32)–C(33)	111 (1)

(c) Proposed Hydrogen Bonds (Å)[b]

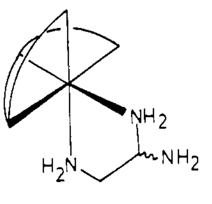
N(1)–H(N1)···O(3a)	3.11 (2)	O(w2)···O(1b$^{\mathrm{IV}}$)	3.03 (3)
N(2)–H(N2)···O(w5$^{\mathrm{I}}$)	2.89 (5)	O(w3)···O(3c)	2.98 (6)
N(31)–H(N31a)···O(2c)	3.12 (2)	O(w5)···O(3c)	3.06 (5)
N(31)–H(N31b)···O(1a)	2.97 (2)	O(w1)···O(w5$^{\mathrm{V}}$)	2.61 (7)
N(32)–H(N32a)···O(1c$^{\mathrm{II}}$)	3.03 (2)	O(w2)···O(w4)	3.02 (5)
N(32)–H(N32b)···O(w3$^{\mathrm{I}}$)	2.96 (4)		
N(32)–H(N32b)···O(w4$^{\mathrm{I}}$)	3.05 (4)		
N(33)···O(w2$^{\mathrm{I}}$)	2.72 (3)	N(33)···O(3a$^{\mathrm{I}}$)	3.19 (2)
N(33)···O(2a$^{\mathrm{III}}$)	3.01 (2)	N(33)···O(2d$^{\mathrm{III}}$)	3.23 (2)

[a] Estimated standard deviations are given in parentheses. [b] Roman numeral superscripts refer to the following equivalent positions relative to *x*, *y*, and *z*: (I) $^1/_2 - x, -y, z - ^1/_2$; (II) $x - 1, y, z$; (III) $x - ^1/_2, ^1/_2 - y, -z$; (IV) $1^1/_2 - x, -y, ^1/_2 + z$; (V) $^1/_2 + x, ^1/_2 - y, 1 - z$.

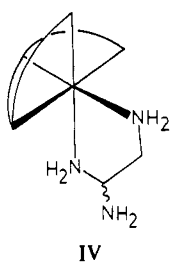
and have shown that a pronounced chiral induction is achieved that should have general application to the synthesis of chiral vicinal diamines. Two major ternary diastereoisomers have been obtained, one of which has been characterized crystallographically. The nature of the other has been elucidated by using NMR techniques.

A perspective drawing of the cation Λ-β_2-[Co(*R*,*R*-picchxn)(tap)]$^{3+}$ is shown in Figure 1, together with the atom-labeling scheme. Atomic coordinates are given in Table I. Dimensions of the metal coordination sphere and the tap ligand, together with a proposed hydrogen-bonding system in the crystal, are given in Table II. The pendant amine group of the triamine is clearly hydrogen bonded to a lattice water molecule and to perchlorate oxygen atoms. All four of the coordinated amine nitrogen atoms also participate in the hydrogen bonding network and are linked to water molecules and/or oxygen atoms of perchlorate ions. The cobalt atom adopts the expected hexacoordination, and the bonding parameters of the Co(*R*,*R*-picchxn) fragment are very similar to those found in analogous complexes.[6,9–11] Because of the inherent chirality of the tetradentate moiety, assignment of absolute configuration is made unambiguous. The Λ-β_2 configuration is confirmed, consistent with its CD and NMR spectra and with those of known analogues.[6,9–11] The tap ligand coordinates as a bidentate moiety to form a five-membered chelate ring with a δ conformation. Thus the triamine is structured by coordination as an internal diastereoisomer and such that the resultant chiral carbon atom has *S* absolute configuration.

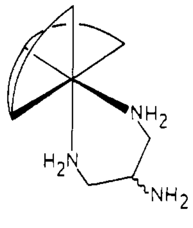
For such a Λ-β-complex with tap coordinated, there are six possible diastereoisomers, as shown in structures III–V. Structures III and IV represent β_1 and β_2 isomers, respectively. The results of the structure analysis show that the first major isomer eluted from the column is the *S* form of structure III.



III



IV



V

The CD spectra of the second isomer, which could not be completely freed of $LiClO_4$, and of the corresponding en complex

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[9] Chambers, J. A.; Goodwin, T. J.; Williams, P. A.; Stephens, F. S.; Vagg, R. S. *J. Coord. Chem.* **1988**, *17*, 277.

[10] Birse, E. F.; Cox, M. A.; Williams, P. A.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1988**, *148*, 45.

[11] Birse, E. F.; Williams, P. A.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1988**, *148*, 63.

Table III. Chemical Shifts (δ), Multiplicities, and Coupling Constants (Hz) for Solutions of the Tap Complexes in D_2O

	Λ-β_2	Λ-β_1
H(11)	8.54, d, 6.0	8.75, d, 6.0
H(12)	7.96, t, ca. 7.0	7.98, t, ca. 7.0
H(13)	8.36, t, ca. 7.5	8.37, t, ca. 7.5
H(14)	7.93, d, 8.0	7.92, d, 8.0
H(21)	7.15, d, 6.0	7.28, d, 6.0
H(22)	7.50, t, ca. 7.0	7.53, t, ca. 7.0
H(23)	8.17, t, ca. 7.5	8.18, t, ca. 7.5
H(24)	7.82, d, 7.7	7.84, d, 7.5
H(16a)	4.72, d, 16.8	4.69, d, 16.0
H(16b)	4.42, d, 16.8	4.49, d, 16.0
H(26a)	4.95, d, 17.3	5.27, d, 18.0
H(26b)	4.49, d, 17.3	4.48, d, 18.0
H(31a)	3.30, dd, 12.8, 4.0	2.97, dd, 12.5, 4.0
H(31b)	2.70, t, 12.8	3.26, t, 12.5
H(32)	3.61, m, 12.8, 6.5, 6.5, 4	3.42, complex
H(33a)	3.32, dd, 14.0, 6.5	ca. 3.5, obscured
H(33b)	3.28, dd, 14.0, 6.5	ca. 3.5, obscured
H(1)	3.37, complex	ca. 3.5, complex
H(2)	2.6, obscured	2.63, td, 11.5, 3.0
H(3a,b)	2.5–2.6 (2 H)	2.52; 2.48; 1.91;
H(4a,b)	1.75–1.9 (3 H)	1.83; 1.78; 1.40;
H(5a,b)	1.3–1.4 (2 H)	1.31; 1.19 (each 1 H)
H(6a,b)	1.18 (1 H)	
C(1)	68.4	68.65
C(2)	74.9	75.0
C(3), C(6)	31.8; 32.3	32.15; 32.6
C(4), C(5)	25.6; 26.2	25.9; 26.6
C(11)	153.1	154.1
C(12)	131.5	131.7
C(13)	145.8	145.8
C(14)	128.3	128.5
C(21)	153.7	154.4
C(22)	129.7	129.8
C(23)	145.0	145.1
C(24)	128.0	128.0
C(15), C(25)	167.5; 163.7	167.4; 164.1
C(16)	55.9	56.1
C(26)	59.5	60.2
C(31)	49.2	49.9
C(32)	58.0	57.1
C(33)	41.6	42.8

indicate that both complexes have Λ absolute configuration. The ^1H NMR spectra in the aromatic region for the three complexes indicate that the tetradentate moiety is coordinated with β geometry (Figure 2), but coordination of tap in the second isomer needs to be ascertained. In the absence of an X-ray structure determination, other NMR experiments were undertaken to clarify this point. Chemical shift and coupling data for the tap complexes are listed in Table III.

The ^1H NMR spectrum of the Λ-β_2 isomer, which aids in the interpretation of that for the other isomer, shows aromatic resonances, which were readily assigned to individual pyridyl protons by using coupling information (decoupling and COSY experiments). Notably, the protons (H(21) and H(11)) adjacent to the two pyridyl nitrogen atoms are at the extremes of the aromatic region, respectively at δ 7.15 and 8.54, demonstrating their different magnetic environments. This results from the two pyridyl rings lying approximately perpendicular to one another such that H(21) is strongly shielded by the other ring. Assignment of the aliphatic region was more difficult, but fortunately a clear, sharp triplet (J = 12.8 Hz) at δ 2.70 (H(31b)) was very useful. Pseudo-INDOR experiments on this triplet showed it to be coupled only to a complex multiplet at δ 3.61 (H(32)) and to a double doublet (J = 12.8, 4 Hz) at δ 3.30 (H(31a)) obscured in the normal spectrum. The protons H(31a) and H(31b) are a geminal pair of the coordinated triaminopropane, and the multiplet thus is attributable to the central methine proton (H(32)) of this unit. A COSY-45 spectrum confirmed these couplings and revealed eventually the coupling connectivity of all the protons in the molecule.

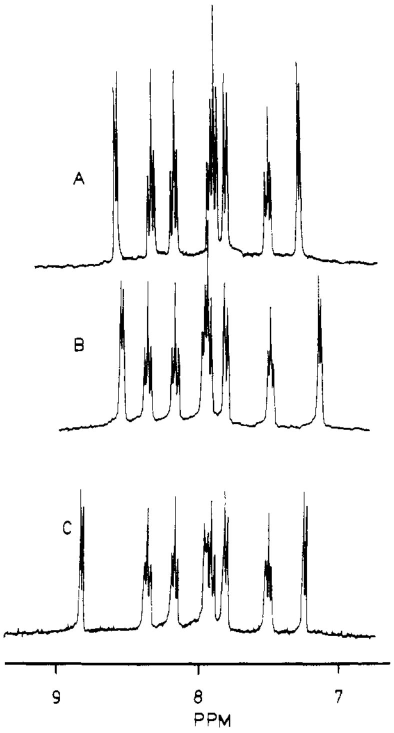

Figure 2. ^1H NMR spectra in the aromatic region of (A) Λ-β-[Co(*R*,*R*-picchxn)(en)]$^{3+}$ and (B, C) Λ-β_2- and Λ-β_1-[Co(*R*,*R*-picchxn)(*S*-tap)]$^{3+}$, respectively, in D_2O.

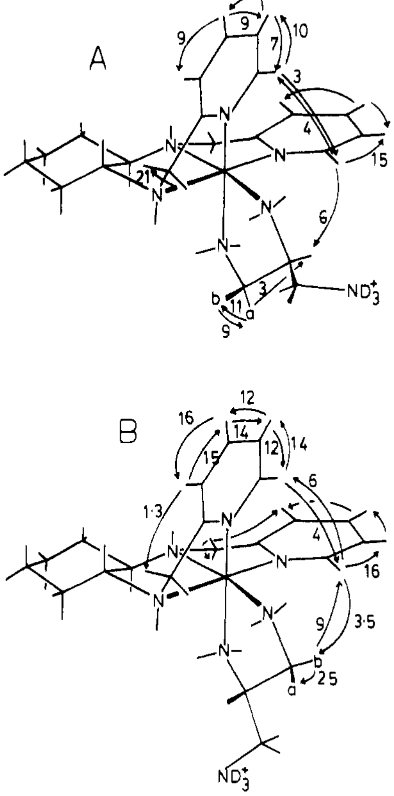

Figure 3. NOE enhancements (%): (A) Λ-β_1- and (B) Λ-β_2-[Co(*R*,*R*-picchxn)(*S*-tap)]$^{3+}$. Arrows with no numerical values refer to significant enhancements for which near-overlap of peaks made integrals uncertain.

A series of difference NOE experiments showed a considerable number of expected enhancements. These are indicated in Figure 3. Especially important is the 3.5% enhancement of the triplet (H(31b)) at δ 2.7 when pyridine proton H(11) is saturated. This establishes that proton H(31b) lies near to this pyridine proton, and hence its geminal partner H(31a) lies away from the pyridine ring. In addition, the coupling constants indicate that the vicinal proton H(32) must lie approximately transoid to H(31b). The orientation of the uncoordinated $-CH_2NH_2$ chain is thereby determined, although its protons (H(33a) and H(33b)) are not clearly separated in the normal NMR spectrum. This stereochemical information on the coordinated triaminopropane unit is therefore completely consistent with the results of the X-ray structure determination.

A corresponding analysis of the ^1H NMR spectrum of the β_1 isomer confirmed its stereochemistry. The atom-numbering system of the β_2 isomer again is used for this molecule, retaining the relative orientations of the protons in the coordinated triaminopropane ligand. The pattern of aromatic resonances (Figure 2) is directly comparable with those of the β_2 isomer and of the en complex and indicates an almost identical arrangement of the tetradentate ligand. The most obvious difference is a small downfield shift for the proton H(11), suggesting that its immediate environment is the only dissimilarity. The pattern of the aliphatic regions for the two tap complexes again are similar with almost identical resonance structures (Table III). The environments most affected would appear to be for the protons H(26a), a small downfield shift, and H(31a) and H(31b) where their resonance positions are interchanged. All the above is consistent with a β_1 structure with the absolute configuration of C(32) still to be defined. Saturation of pyridine proton H(11) gave no NOE enhancement of H(31b) but a 6% enhancement of proton H(32) (Figure 3). This establishes unambiguously the *S* absolute configuration of the coordinated triaminopropane ligand, the same as in the β_2 isomer.

The ^{13}C NMR spectra of the two isomers confirm the relative orientations of the methylene and methine carbon atoms in these two structures. This was accomplished by using broad-band proton decoupling and the DEPT method. The two-dimensional CH correlation sequence XHCORRD was used to correlate the ^{13}C chemical shifts with the ^1H chemical shifts. The shifts for the two isomers are very similar and in accordance with expected values. In each isomer the methine protons (H(32)), which appear at δ 3.61 and 3.42, couple to the C(32) carbons at δ 58.0 and 57.1, respectively. Slight torsional changes in the tetradentate moiety caused by the relative orientations of the triamine are reflected in the small differences observed in their spectra.

Although the two major products were isolated and characterized separately, for synthetic application involving reaction of the pendant amine group, such a separation would not be necessary. Both complexes, representing greater than 80% synthetic yield, contain the tap ligand with *S* absolute configuration. Thus, having started with a prochiral potentially terdentate ligand, we have achieved a nearly absolute chiral induction in forcing it to adopt a bidentate coordination mode. The situation is inherently different from that involving aminomalonic acid complex analogues;[6,9-11] any reaction of the pendant amine of the tap ligand would not alter the chirality of the methine carbon atom whereas for the aminomalonates decarboxylation involves the chiral carbon atom. Hence this tap system represents a possible novel route to the synthesis of optically pure chiral vicinal diamines. The system may be applied to other related prochiral triamines with the possibility of easy removal of the chiral product from the complex by a reported electrochemical procedure.[12]

It is of interest that the only species that could be effectively isolated contain the tap ligand coordinated in an *S* configuration. Molecular models and the present structure determination suggest no particular steric reason for this. It is worthy of note that repeated syntheses of the complexes give the same mixture of diastereoisomers.

Experimental Section

All materials used were of reagent grade. Λ-β-[Co(*R*,*R*-picchxn)Cl_2]$ClO_4\cdot{}^1/_2H_2O$ was synthesized as described previously.[13] (*Caution!* perchlorate salts of complex ions can be explosive and must be handled with care. However, we have not experienced any problems with the salts described herein.) 1,2,3-Triaminopropane was prepared by using the method of Henrick et al.[14] (Caution! the preparation of the amine from glycerol proceeds via the triazide, which is potentially explosive. We experienced no problems with this preparation, but as a precaution, the crude triazide was dissolved in ethanol and reduced immediately. The product was isolated by evaporation of its solution in dichloromethane.)

Λ-β-[Co(*R*,*R*-picchxn)(en)]$(ClO_4)_3\cdot 2H_2O$. To a suspension of Λ-β-[Co(*R*,*R*-picchxn)Cl_2]$ClO_4\cdot{}^1/_2H_2O$ (0.535 g, 1 mmol) in water (50 cm^3) was added en·2HCl (0.665 g, 5 mmol) and aqueous 1.0 M NaOH (4 cm^3). The mixture was stirred and heated at 65 °C for 1 h. The resulting bright orange solution was cooled to room temperature, diluted 5-fold with H_2O, and applied to a CM Sephadex C25 column (2 × 100 cm) in the Na^+ cycle, which was then flushed with H_2O. Elution of the column with 0.3 M NaCl developed two yellow-orange bands. The first eluted contained a negligible amount of complex and was discarded. The slower moving band contained a single isomer. Fractions were combined, reduced to a small volume, and filtered. The filtrate was saturated with $NaClO_4$ and enough ethanol added to induce cloudiness. During 3 days the product crystallized as bright orange, equant prisms (yield: 0.31 g). Anal. Calcd for $C_{20}H_{36}N_6Cl_3O_{14}Co$: C, 32.0; H, 4.8; N, 11.2. Found: C, 32.2; H, 5.0; N, 11.1. Characteristic spectral data (H_2O): $\lambda_{max} = 469$ nm, $\epsilon = 170\ M^{-1}\ cm^{-1}$; CD (extremum), $\Delta\epsilon(471\ nm) = +2.03\ M^{-1}\ cm^{-1}$.

Λ-β_2-[Co(*R*,*R*-picchxn)(*S*-tap)]$(ClO_4)_3\cdot 3H_2O$. To a suspension of Λ-β-[Co(*R*,*R*-picchxn)Cl_2]$ClO_4\cdot{}^1/_2H_2O$ (0.535 g, 1 mmol) in H_2O (50 cm^3) was added tap·3HCl (1.085 g, 5 mmol) and aqueous 1.0 M NaOH (6 cm^3). The mixture was stirred and heated at 65 °C for 2.5 h (heating at higher temperatures results in decomposition). The resulting bright yellow-orange solution was chromatographed as above (3 × 200 cm column) by using aqueous 0.4 M $LiClO_4$ as eluant. Three yellow-orange bands were completely resolved and removed from the column by using aqueous 1.0 M $LiClO_4$. Each band was collected in fractions, and electronic and CD spectral measurements showed the first two bands, containing approximately equal amounts of complex, to each consist of a single isomer. The third band, which represented less than 10% of the total yield, based on Co, contained more than one isomer, but this mixture was not investigated further.

The fractions from the first eluted band were combined and the solvent removed in vacuo. The residue was dissolved in a minimum of hot ethanol, and crystals of the product formed from the cooled solution during a 24-h period. These were collected at the pump, washed with ethanol, and air-dried (yield: 0.11 g, 42%, with the total yield of this isomer determined from spectroscopic measurements on the combined fractions). Anal. Calcd for $C_{21}H_{41}N_7Cl_3O_{15}Co$: C, 31.6; H, 5.2; N, 12.3. Found: C, 31.6; H, 5.0; N, 11.9. Characteristic spectral data (H_2O): $\lambda_{max} = 471$ nm, $\epsilon = 188\ M^{-1}\ cm^{-1}$; CD (extremum), $\Delta\epsilon(473\ nm) = +2.23\ M^{-1}\ cm^{-1}$.

Λ-β_1-[Co(*R*,*R*-picchxn)(*S*-tap)]$(ClO_4)_3\cdot n LiClO_4\cdot x H_2O$. Fractions from the second major orange band were combined and reduced to dryness in vacuo. Attempts to obtain the pure complex salt, by using a procedure similar to that for the β_2 complex, were unsuccessful. Nor did it prove possible to crystallize it pure with a variety of other counterions; the material was always contaminated with $LiClO_4$, and it has proven thus far impossible to desalt completely. The compound was, however, NMR pure. Anal. Calcd for $C_{21}H_{35}N_7O_{12}Cl_3Co$ (i.e., the anhydrous perchlorate of the pure complex): C, 34.0; N, 13.2; Co, 7.9. Found: C, 24.0; N, 9.4; Co, 5.6. From this analysis Co:C:N = 1:21.0:7.1, substantiating the above stoichiometry. On the basis of the Co analysis, the compound is 70.9% pure; the remainder comprises $LiClO_4 + H_2O$ (total yield 49%, based on Co analysis of the mixture). Characteristic spectral data (H_2O): $\lambda_{max} = 472$ nm, $\epsilon = 183\ M^{-1}\ cm^{-1}$; CD (extremum), $\Delta\epsilon(477\ nm) = +1.96\ M^{-1}\ cm^{-1}$.

X-ray Structural Analysis. A sample of Λ-β_2-[Co(*R*,*R*-picchxn)(*S*-tap)]$(ClO_4)_3\cdot 3H_2O$ was recrystallized from aqueous acetone to yield needles, many of which were twinned, as revealed by precession photographs. The single crystal selected for the structure determination proved to be highly mosaic. Crystal data: $C_{21}H_{41}N_7Cl_3O_{15}Co$, $M_r = 796.9$, orthorhombic, $a = 9.157$ (10) Å, $b = 16.969$ (18) Å, $c = 22.497$ (22) Å, $V = 3495.7$ Å^3, $Z = 4$, $D_c = 1.514$ Mg m^{-3}, $F(000) = 1656$, μ(Mo Kα) = 8.2 cm^{-1}, space group $P2_12_12_1$ (No. 19).

Unit cell parameters were initially determined from single-crystal precession photographs by using Mo Kα radiation and refined via a least-squares fit to diffractometer data. Intensities were collected in a ω-2θ scan mode for the range $5° < 2\theta < 60°$ at 20 °C on a Hilger and Watts Y290 four-circle diffractometer using Mo Kα radiation and a

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solid-state detector, the latter eliminating the need for beam monochromatization. Measurement of a standard reflection showed no variation greater than 2 standard deviations throughout, and hence there was no evidence of crystal decay. In a number of cases, 2-4 equiv were measured for particular reflections. In the few cases where significant differences occurred, the reflections concerned were assessed individually. Intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. The crystal used for data collection could be inscribed in a rectangular block of dimensions 0.19 × 0.23 × 0.30 mm, but part of the surface was curved and it was not possible to use any of the standard routines for calculating absorption factors. It is thought that the low μ and the reasonable regularity of the dimensions means that the absence of absorption corrections has not seriously affected the structural details obtained. A total of 4040 reflections were measured, which after averaging gave 3498 unique reflections of which 2126 had $I > 3\sigma(I)$ and these were used for the structural analysis.

The structure was solved by the heavy-atom method and refined in three block matrices by using least-squares procedures which minimized the function $\sum w\Delta^2$. The weight for each reflection, w, in the final cycles of refinement is given by $w = (5.0 + 0.5|F_o| + 0.006|F_o|^2)^{-1}$. For this scheme average values of $\sum w\Delta^2$ for ranges of increasing $|F_o|$ were nearly constant. A difference map revealed one of the perchlorate ions and two of the lattice water molecules to be disordered. Occupancies for partial atoms were assigned on the basis of peak heights in the difference map. After isotropic refinement a further difference map yielded the approximate positions for the hydrogen atoms of the cation with the exception of those attached to N(33), the pendant nitrogen atom of the coordinated triamine. Attempts to locate these hydrogen atoms or those of the water molecules during subsequent refinement were unsuccessful nor could they be positioned unambiguously by calculation. The positions of the other hydrogen atoms were optimized, assuming C-H and N-H to be 1.0 Å and assuming the appropriate geometry of the atom to which they are bonded. The anisotropic refinement process was terminated when the minimization factor changed by <0.1% and a final difference map showed no residual electron density greater than |0.5| e Å^{-3}. The final R was 0.078 and R' [$=(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$] was 0.107.

The structural solution and analysis calculations were carried out on a FACOM M340S computer using programs written by F.S.S. Neutral-atom scattering factors, corrected for anomalous dispersion, were taken from ref 15. The final atomic coordinates for non-hydrogen atoms are given in Table I, and selected interatomic parameters are presented in Table II.

Physical Measurements. Electronic and CD spectra were recorded by using a Perkin-Elmer Lambda 5 spectrophotometer and a Jobin-Yvon CNRS Dichrographe III instrument, respectively. AAS measurements were carried out on a Varian AA 274 instrument. NMR spectra of samples dissolved in D_2O were recorded at 360 MHz for ^1H and at 90 MHz for ^{13}C by using a Bruker WM 360 spectrometer at 21 °C, with standard Bruker software. Chemical shifts (δ) are given in ppm relative to TPS as internal standard.

Nuclear Overhauser effects (NOE's) were measured by the difference method. Low-intensity presaturation pulses (3 s) were applied before each acquisition (16K data points over 3300 Hz, 90° observation pulse, 10-s relaxation delay), accumulating 40 sets of data, each containing two "dummy" scans and eight acquired scans for each irradiation position and a "blank" position. A line-broadening of 1 Hz was applied to the subtracted FID's before Fourier transformation. Quantitative values for the enhancements were determined from integrals, wherever possible. Pseudo-INDOR effects were determined in a similar way, but with an observation pulse of 30° and the irradiation power reduced by 20 db. ^1H COSY-45 spectra were measured by using 2K data points over 3300 Hz in f_2 and 512 points zero-filled to 1K in f_1. $^{13}C-^1H$ correlation was carried out by using the Bruker XHCORRD routine optimized for a coupling constant of 135 Hz, collecting 1K data points over 14500 Hz in f_2 and 256 points in f_1 with zero-filling in both dimensions.

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Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and complete molecular dimensions and contact distances (6 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Contribution from the Dipartimento di Chimica
e Chimica Industriale, Sezione Chimica Inorganica,
Università di Pisa, via Risorgimento 35,
I-56126 Pisa, Italy, and Institut für Anorganische
Chemie der Universität Tübingen, Auf der
Morgenstelle 18, D-7400 Tübingen, Germany

Deoxygenation of Carbon Dioxide to Diethylformamide in the Zn/HNEt$_2$/CO$_2$ System. Crystal and Molecular Structure of [Zn$_4$O(O$_2$CNEt$_2$)$_6$]

Antonio Belforte,[†] Fausto Calderazzo,*,[†] Ulli Englert,[†]
and Joachim Strähle[‡]

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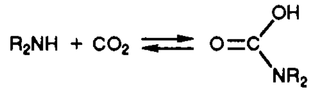
Carbon dioxide chemistry is an active field of research, and much interest is devoted to the use of metal systems to modify its reactivity.[1] Energy demanding transformations such as the carbon dioxide deoxygenation (1), can be realized, for example,

$$CO_2 + 2e^- \rightarrow CO + O^{2-} \qquad (1)$$

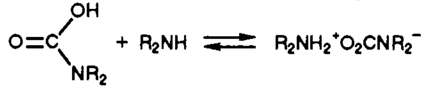
when the reducing equivalents are provided by a metal, either in a heterogeneous system[2] or as part of a soluble coordination compound.[3] Metals themselves[2,3] can also act as oxygen acceptors, the formation of a metal-oxygen bond thus controlling the overall thermodynamic balance.[2-4]

Metal carbamato complexes, [M(O$_2$CNR$_2$)$_n$], can be readily prepared from carbon dioxide and a metal precursor in the presence of a secondary amine. In recent years, we became interested in the chemistry of these compounds, and in addition to synthetic and structural aspects,[5] we pointed out their utility for accomplishing incorporation[6] and deoxygenation[7] reactions of carbon dioxide. In continuation of these studies, we decided to prepare the still unknown homoleptic zinc(II) dialkylcarbamato complexes. Since usual synthetic techniques, such as the reaction of metal chlorides with the CO$_2$/HNR$_2$ system[5] or the formal CO$_2$ insertion into the M-NR$_2$ bond,[8] proved to be unsuitable,[9] a different method of preparation became necessary.

The alternative method of preparing *N,N*-dialkylcarbamato complexes from metal hydrides[10] or from metal-alkyl precursors[11] can be regarded as a proton abstraction from HOC(O)NR$_2$ or from NH$_2$R$_2^+$O$_2$CNR$_2^-$, both arising from equilibria 2 and 3,



$$R_2NH + CO_2 \rightleftharpoons O{=}C(OH)NR_2 \qquad (2)$$



$$O{=}C(OH)NR_2 + R_2NH \rightleftharpoons R_2NH_2^+O_2CNR_2^- \qquad (3)$$

respectively. We therefore reasoned that zinc metal itself might be able to carry out an electron transfer to the protic reagents present in the R$_2$NH/CO$_2$ system, leading finally to the required homoleptic zinc(II) *N,N*-dialkylcarbamato derivatives. However, we soon realized that, while this was the fundamental reaction pathway, a deoxygenation reaction of CO$_2$ was also occurring.

We here report the results of these studies and the X-ray crystal structure of a tetranuclear μ_4-oxo diethylcarbamato complex of zinc(II) formed in the Et$_2$NH/CO$_2$/Zn system.

Experimental Section

All of the operations were carried out under an inert atmosphere, or under CO or CO$_2$, as specified. Carbon oxides (CO and CO$_2$) were purchased as high-purity gases and used as such; labeled $^{13}CO_2$ was prepared by decomposing Ba^{13}CO$_3$ (CEA, 90% enriched) with concentrated sulfuric acid. HNEt$_2$ was distilled from sodium-potassium alloy and kept over sodium sand. Metallic zinc powder was etched with con-

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[†] Università di Pisa. Present address of A.B.: Solvay SpA, I-57016 Rosignano Solvay, Livorno, Italy. Present address of U.E.: Institut für Anorganische Chemie der RWTH, Professor-Pirlet-Strasse, D-5100 Aachen, Germany.

[‡] Universität Tübingen.

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