Trigonal Prismatic Geometry with Non-rigid Ligands: Cobalt(II) Complexes of Triaza-macrocycles with Pendant Alcohol Arms

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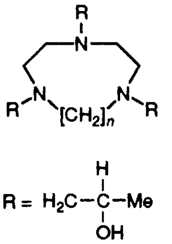
The crystal structures of two cobalt(II) complexes with fully saturated non-rigid ligands show that the cobalt(II) ions have trigonal prismatic coordination.

Transition metal complexes with trigonal prismatic coordination geometry are rare,[1] the vast majority of six-coordinate species being octahedral or pseudo-octahedral. The two principal reasons[2,3] why the octahedron is favoured over the trigonal prism are: (*i*) the larger ligand-field stabilisation energy (LFSE) of octahedral complexes compared with the analogous trigonal prismatic species (except for d^0, d^1, d^{10}, high spin d^5 and d^6 and low spin d^2) and (*ii*) the greater inter ligand repulsion of the trigonal prism compared with the octahedron. Most of the reported examples of first row transition metal complexes with trigonal prismatic geometry are of metal ions with d^0, d^{10} or high spin d^5 configurations. For these configurations there is no LFSE preference and the steric requirements of ligands (or crystal packing forces) will dominate coordination geometry. Where trigonal prismatic geometry has been observed in complexes of ions with an LFSE preference in favour of octahedral geometry it is dictated by ligand systems containing rigid donor atom arrays, which cannot distort to provide octahedral coordination.[4,5] Recently trigonal prismatic geometry has been observed for d^0 systems with six pure σ donors, which undergo second order Jahn–Teller distortions.[6]



$R = H_2C-\overset{H}{\underset{OH}{C}}-Me$

H_3L^1, *n* = 2
H_3L^2, *n* = 3
H_3L^3, *n* = 4
H_3L^4, *n* = 5

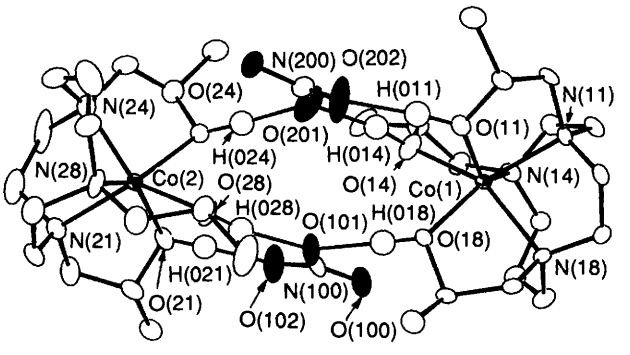


Fig. 1 Molecular structure and atomic labelling scheme for $[(Co\{H_3L^2\}_2(NO_3)_2][PF_6]_2$ **1** (H_3L^2 is the *R* enantiomer) with thermal parameters shown at the 20% probability level. The oxygen atoms of the bridging nitrate ions are coloured black. Important bond lengths (Å) and angles (°) (given for unit 1 only) are: Co(1)–O(11) 2.145(7), Co(1)–O(14) 2.101(7), Co(1)–O(18) 2.089(6), Co(1)–N(11) 2.147(7), Co(1)–N(14) 2.160(8), Co(1)–N(18) 2.204(7), O(11)–Co(1)–O(14) 84.5(3), O(11)–Co(1)–O(18) 82.8(3), O(14)–Co(1)–O(18) 85.0(3), N(11)–Co(1)–N(14) 82.4(3), N(11)–Co(1)–N(18) 81.0(3), N(14)–Co(1)–N(18) 94.9(3).

In this communication we present the structural characterisation of what we believe to be the first examples of trigonal prismatic Co^{II} with saturated non-rigid ligands.

We have done extensive work[7–9] on the coordination chemistry of the hexadentate pendant arm macrocyclic ligand *N,N′,N″*-tris-(2*R*)-2-hydroxypropyl-1,4,7-[9]aneN$_3$, H_3L^1. In order to investigate the effect of increasing steric strain in pendant-arm macrocyclic systems we have prepared a series of analogous ligands by expanding the macrocycle ring. We have prepared and structurally characterised the Co^{II} complexes of three such ligands: H_3L^2, H_3L^3 and H_3L^4. We present the detailed crystal structure of the Co^{II} complexes of H_3L^2 and H_3L^4 and briefly discuss the structure of the Co^{II} complex of H_3L^3.

The Co^{II} complex of H_3L^2 crystallises as a nitrate-bridged dimer $[(Co\{H_3L^2\})_2(NO_3)_2][PF_6]_2$ **1**, whose structure† is illustrated in Fig. 1. The dimer is formed from two crystallographically distinct $[Co^{II}(H_3L^2)]^{2+}$ subunits linked by two hydrogen bonded nitrate ions. The nature of the nitrate bridging units is most unusual, being a very rare mode of hydrogen bonding for nitrate ions. Views of ball-and-stick models of the subunits, as seen down the pseudo-three-fold axes perpendicular to the N_3 planes, are presented in Fig. 2. The trigonal prismatic geometry of both subunits is apparent, the average twist of the two triangles of ligators away from the

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† *Crystal data* for **1**: $C_{16}H_{35}CoF_6N_4O_6P$, *M* = 583.38, triclinic, space group *P*1 (No. 1, C^1_1), *Z* = 2, *a* = 8.5064(9), *b* = 9.764(3), *c* = 15.311(2) Å, α = 83.71(2), β = 89.531(2), γ = 74.624(2)°, *U* = 1218.5(5) Å^3, D_c = 1.59 g cm^{-3}, *F*(000) = 606, μ(Mo-Kα) = 8.48 cm^{-1}. The structure was solved by direct methods and subsequent electron density difference synthesis, and was refined by full matrix least squares using 3981 absorption/extinction (DIFABS) corrected data. A total of 4611 unique data were measured on a CAD4F automatic diffractometer with graphite monochromated X-radiation (λ = 0.71069 Å) using θ/2θ scans. The final $R(R_w)$ values were 0.052 (0.068) for a total of 323/142/215 parameters in three blocks (due to matrix size limitations) and $[\sigma^2(F_o)]^{-1}$ weights. Hydrogen atoms (except the OH hydrogens) were incorporated at fixed positions with C–H = 1 Å. The position of the OH hydrogen atoms was determined from a difference Fourier. The correctness of the enantiomer was confirmed by refinement of η, the anomalous scattering factor, which refined to a value of 0.86(7). Refinement using the inverted configuration converged with higher residuals of $R(R_w)$ 0.054 (0.072).

Crystal data for **2**: $C_{18}H_{39}CoN_5O_9$, *M* = 528.47, orthorhombic, space group $P2_12_12_1$ (No. 19, D^4_2), *Z* = 4, *a* = 10.1895(6), *b* = 11.632(1), *c* = 20.309(1) Å, *U* = 2407.1(3) Å^3, D_c = 1.458 g cm^{-3}, *F*(000) = 1120, μ(Mo-Kα) = 7.64 cm^{-1}. The structure was solved by direct methods and subsequent electron density difference synthesis, and was refined by full matrix least squares using 3662 absorption/extinction (DIFABS) corrected data. A total of 4861 unique data were measured on a CAD4F automatic diffractometer with graphite monochromated X-radiation (λ = 0.71069 Å) using θ/2θ scans. The final $R(R_w)$ values were 0.047 (0.067) for a total of 299 parameters and $[\sigma^2(F_o)]^{-1}$ weights. Hydrogen atoms (except the OH hydrogens) were incorporated at fixed positions with C–H = 1 Å. The position of the OH hydrogen atoms was determined from a difference Fourier. The correctness of the enantiomer was confirmed by refinement of η, the anomalous scattering factor, which refined to a value of 1.05. Refinement using the inverted configuration converged with higher residuals of $R(R_w)$ 0.056 (0.079).

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

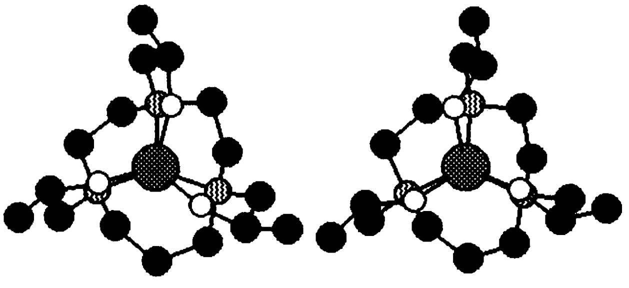

Fig. 2 View of the two halves of **1** looking, in each case, down the pseudo-three-fold axis perpendicular to the N_3 plane

eclipsed configuration being 7.5 and 12° for units 1 and 2, respectively. The exocyclic and endocyclic chelate rings are in the same (λ) conformation. This has been observed in other complexes with trigonal prismatic coordination, such as the $[Mn^{II}(H_3L^1)]^{2+}$ unit of $[Mn^{II}(H_3L^1)(L^1)Mn^{IV}]^{3+}$[8] and the $[Zn^{II}(H_3L^1)]^{2+}$ unit of $[Zn^{II}(H_3L^1)(L^1)V^{IV}]^{3+}$[9] and may be contrasted with the ring conformations in the pseudo-octahedral Mn^{IV} and V^{IV} units in the above complexes and in $[Co^{III}(H_3L^1)(L^1)Co^{III}]^{3+}$,[7] where the endocyclic and exocyclic chelate rings are of opposite conformation. The two $[Co^{II}(H_3L^2)]^{2+}$ units in **1** have opposite absolute configurations despite both containing chelate rings with the same, *R*, methyl substituents. Thus the twist away from trigonal prismatic geometry is left handed (Λ) around Co(1) and right handed (Δ) about Co(2).

While the trigonal prismatic coordination at cobalt is presumably imposed by the H_3L^2 ligand it is worth noting that H_3L^2 *is* capable of supporting near-octahedral coordination. We have prepared and structurally characterised[10] an (Mn^{II}, Mn^{IV}) hydrogen bridged dimer of H_3L^2. The structure is similar to that of $[Mn^{II}(H_3L^1)(L^1)Mn^{IV}]^{3+}$[8] (although the two and three carbon bridges of the ring are disordered) and, as in that complex, the Mn^{II} centre is trigonal prismatic while the Mn^{IV} centre is pseudo-octahedral.

The structure† of the cation of the monomeric complex $[Co(H_3L^4)][NO_3]_2$ **2** is shown in Fig. 3. Again the stereochemistry at the Co^{II} is best described as trigonal prismatic although the C_5 bridge prises back two of the nitrogen ligators. Thus while the three O–Co–O angles are similar, the N(4)–Co–N(10) angle (116.5°) is much larger than the other two N–Co–N angles (80.4 and 80.8°). As a consequence of this, the O_3 set of ligators is not twisted away from the N_3 set in either a right or left handed sense but N(1) and O(1) are almost eclipsed while O(4) is twisted in a counter clockwise direction from N(4) and O(10) in a clockwise direction from N(10).

We have also determined[10] the structure of the Co^{II} complex with H_3L^3. The stereochemistry at Co^{II} is half way between trigonal prismatic and octahedral (average twist of 31°).

All three Co^{II} complexes are air-stable and display resistance to chemical oxidation to the corresponding Co^{III} species. This is in contrast to the Co^{II} complex of H_3L^1, $[Co(H_3L^1)]^{2+}$ which is highly air-sensitive and is rapidly oxidised to the hydrogen-bridged dimer $[Co^{III}(H_3L^1)(L^1)Co^{III}]^{3+}$[6] by molecular oxygen. Although we have not determined the structure of $[Co(H_3L^1)]^{2+}$ it is reasonable to assume that it has pseudo-octahedral coordination at Co^{II}.

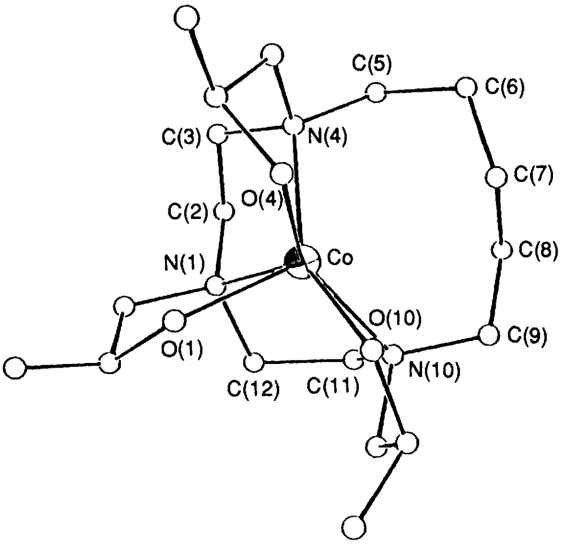

Fig. 3 Molecular structure and atomic labelling scheme for $[Co(H_3L^4)][NO_3]_2$ **2** (H_3L^4 is the *S* enantiomer). Important bond lengths (Å) and angles (°) are: Co–O(1) 2.108(4), Co–O(4) 2.135(4), Co–O(10) 2.177(4), Co–N(1) 2.224(4), Co–N(4) 2.282(4), Co–N(10) 2.167(4), O(1)–Co–O(4) 80.7(2), O(1)–Co–O(10) 82.4(2), O(4)–Co–O(10) 78.5(2), N(1)–Co–N(4) 80.4(2), N(1)–Co–N(10) 80.8(2), N(4)–Co–N(10) 116.5(2).

An examination of the bond angles in the larger chelate rings of **1** and **2** reveals considerable distortion of the ligand backbones. Molecular mechanics studies indicate that distortions of bond angles are of relatively low energy compared to distortions of bond lengths.[11] However considering the number of bonds in these complexes the total strain energy must be larger.

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