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# Molecular mechanics and chemical reactivity. A model study of steric effects influencing Co(III) phosphate ester hydrolysis

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## Contents

## Abstract

The use of molecular mechanics for the study of Co(III) metal complexes is discussed with emphasis on the investigation of a model system for probing aspects of Co(III)-catalysed phosphate ester hydrolysis. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Molecular mechanics; Strain energy; Phosphate ester; Hydrolysis; Molecular modelling

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## 1. Introduction

It is now more than 50 years since attempts to calculate molecular strain energies were first attempted. In 1946, one of the earliest quantitative estimates of steric strain energy was undertaken by Ingold et al. in order to rationalise the unexpected slow rate of nucleophilic substitution of a series of neopentyl bromide compounds [1]. The fact that steric effects in chemical systems may profoundly influence their kinetic behaviour had long been recognised. The strain energies (including van der Waals, electrostatic and 'atomic interpenetration' terms) of hypothetical transition state structures were calculated and a comparison made with the values obtained using the same procedure for related, less-branched alkyl bromides. While the calculations involved a considerable degree of parameterisation, the observed experimental effect was so marked that quantitative precision in the calculations was not required to confirm a steric origin for the behaviour.

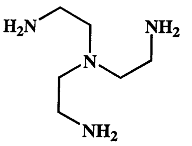
From about this time, other workers, including Westheimer [2], employed related calculations in order to interpret observed kinetic phenomena involving organic systems (for example, the racemisation rates for chiral species) in terms of corresponding calculated transition state structures. Many other studies followed, aided by the development of improved expressions [3,4] and procedures [5,6] for the quantitative evaluation of strain energies.

In an initial attempt to calculate the strain energy of metal-containing structures, Corey and Bailar [7] investigated the stereochemistry of the five-membered chelate rings in bis- and tris-chelate amine complexes of Co(III). Using previously developed hydrogen–hydrogen potential functions [4], they were able to estimate the energy differences between the respective systems having $\delta$ and $\lambda$ conformations of their chelate rings. Ten years on in 1969, Gollogly and Hawkins [8] reinvestigated the above chelate systems more thoroughly, employing a more general force field which, in part, was based upon the many developments that had occurred in molecular mechanics analyses over the previous decade. Since that time, the application of molecular mechanics to the study of Co(III) coordination compounds has become increasingly widespread [9] and has included many investigations where the calculations were performed in order to help elucidate the nature of observed kinetic behaviour by the complexes studied [10].

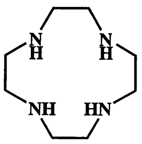
Historically, the substitutionally inert character of Co(III) has given this ion a prominent position in the study of metal coordination stereochemistry. A wide range of well characterised isomeric and other structures have been available which have permitted generally accurate *structural* calibration of molecular mechanics force field parameters for modelling Co(III) complexes [11] while calibration in terms of *energies* has been of somewhat lower reliability [12]. In general, the calculations have also been aided by the tendency of Co(III) to prefer a regular octahedral coordination geometry; this simplifies the development of force field parameters having wider applicability than is possible when a more 'flexible' central metal ion is present [13]. Aspects of the results from molecular mechanics investigations of Co(III) coordination complexes have also been presented in previous reviews [14,15].

## 2. Phosphate ester hydrolysis

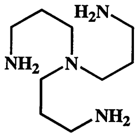
There has been considerable interest in the use of Co(III) species for promoting phosphate ester hydrolysis [16–18]. For example, this interest has extended to the development of catalysts that are capable of specifically cleaving the phosphate diester linkages within DNA [19,20] and cAMP [21]. Hydrolytic cleavage of phosphate diesters promoted by aquahydroxo(tetraamine)cobalt(III) complexes has shown rate enhancements of up to $10^{10}$ over the uncatalysed rate — comparable to the rates with natural phosphodiesterases [21–23]. A feature of the activation is that the hydrolysis rate is quite sensitive to the nature of the tetraamine ligand structure in the Co(III) complex. For example, the complexes $[Co(tren)(H_2O)(OH)]^{2+}$ [tren is tris(2-aminoethyl)amine, **1**], $[Co(cyclen)(H_2O)(OH)]^{2+}$ (cyclen is 1,4,7,10-tetraazacyclododecane, **2**), and $[Co(trpn)(H_2O)(OH)]^{2+}$ [trpn is tris(3-aminopropylamine)amine, **3**] hydrolyse bisnitrophenylphosphate (BNPP) at the respective relative rates of 1:58:312 (pH 7.0, 50°C) [24].



**1; tren**

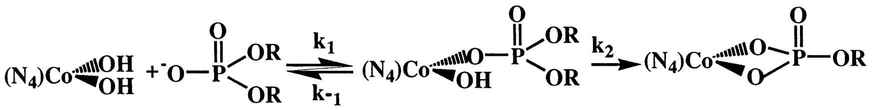


**2; cyclen**



**3; trpn**

Mechanistic investigations of the nature of the rate enhancements have demonstrated (see below) that the reaction proceeds via a four-membered ring intermediate containing the phosphate ester coordinated to the metal centre. Presumably, the adjustment required of the tetraamine ligand to accommodate the strained (four-membered) ring structure governs its formation and, as a consequence, influences the rate of ester hydrolysis [25]. With respect to this Chin et al. [24] have proposed the following scheme for phosphate ester hydrolysis catalysed by the above aquahydroxo(tetraamine)Co(III) complexes:



Constant $k_2$, corresponding to an intramolecular nucleophilic step to yield the four-membered ring species, was found to be very sensitive to the structure of the tetraamine ligand. It was concluded by Chin et al. [24] that a major factor in stabilising the four-membered chelate ring formed is an increase in the bond angle opposite to this ring in the coordination shell of the Co(III).

In view of this, it appeared feasible to apply molecular mechanics to the modelling and prediction of structure–reactivity patterns for Co(III) complexes that are capable of catalysing phosphate ester hydrolysis in the manner discussed.

In the present study a molecular mechanics investigation of model Co(III) $N_4$-amine complexes containing a single four-membered (carbonato) ring has been carried out. In accordance with the approach adopted by Chin et al. [24] which was based on the availability/determination [25] of suitable X-ray structural data, Co(III) species in which the four-membered chelate rings were formed by bidentate carbonato groups were employed as model compounds in our calculations discussed below.

## 3. The MOLMEC package

MOLMEC [26], the minimisation program used in this work, incorporates a local adaptation of the MM2 force field of Allinger [27]. We have previously employed MOLMEC for the development of force field parameters for both low-spin [29] and high-spin [30] Ni(II) bound by $N_4$-donor macrocyclic ligands. The organic parameters used in the force field derive directly from Allinger's original work [28]. Parameters involving Co(III) were taken from our previously published investigations [31,32], although parameters for Co(III) interacting with nitrate and carbonate were developed for the present study [this involved calibration against a range of Co(III) complex structures taken from the Cambridge Crystallographic Data Base containing these anionic ligands]; the new parameters are listed below:

Co(III) nitrate terms
  Stretching constants:
    Co(III)–N(nitro): $K_{str} = 1.950$ N m$^{-1}$ molecule$^{-1}$; $r_0 = 2.25$ Å

  Bending constants:
    N(nitro)–Co(III)–N(nitro): $K_{bend} = 1.500$ Å rad$^{-2}$ molecule$^{-1}$
      $\phi_1 = 90.0,\ \phi_2 = \phi_3 = 0.00$
    N(nitro)–Co(III)–N(amine): $K_{bend} = 1.200$ Å rad$^{-2}$ molecule$^{-1}$
      $\phi_1 = 90.0,\ \phi_2 = \phi_3 = 0.00$

  Torsional constants:
    All torsions involving N(nitro) were set to zero.

Co(III) carbonato terms
    Co(III)–O(carbonato): $K_{str} = 1.950$ N m$^{-1}$ molecule$^{-1}$; $r_0 = 2.80$ Å

  Bending constants:
    O(carbonato)–Co(III)–O(carbonato): $K_{bend} = 0.150$ Å rad$^{-2}$ molecule$^{-1}$
      $\phi_1 = 70.0,\ \phi_2 = \phi_3 = 0.00$
    Co(III)–O(carbonato)C(carbonato): $K_{bend} = 0.050$ Å rad$^{-2}$ molecule$^{-1}$
      $\phi_1 = 85.0,\ \phi_2 = \phi_3 = 0.00$
    O(carbonato)–Co(III)–N(amine): $K_{bend} = 0.050$ Å rad$^{-2}$ molecule$^{-1}$
      $\phi_1 = 90.0,\ \phi_2 = \phi_3 = 0.00$

Torsional constants:
All torsions involving Co(III)–carbonato were set to zero

It is noted that recently [12] a comparative evaluation of five force fields, currently used for modelling Co(III) complexes, has been published. The evaluation included the MOLMEC program which, for example, was shown to be the most accurate of the five for calculating N–Co–N bond angles in Co(III) complexes.

All calculations were carried out on a DEC Station 5000 workstation; the convergence criterion for minimisation was taken to be $\Delta H_{\text{steric}} < 10^{-7}$ kJ mol$^{-1}$ between successive iterations. Likely refinement to a global potential energy minimum (rather than saddle points) was promoted in all cases by the use of a range of 'randomly shaken' starting geometries for each structure calculation.

The atom coordinates from each 'final' MM2 structure were then used as the 'starting' coordinates for re-minimisation using density functional theory (DFT) calculations. The DFT calculations were run using either GAUSSIAN 94 [33] or DFCALC[1]; the gradient converted non-local method DP86 [34,35] was employed. In all cases 6-311G* basis sets were utilised. Calculations were run on a SGI Power Challenge computer system; typically, each minimisation required several days of CPU time. Happily, the final geometries obtained by the MM2 and DFT procedures for individual complexes were quite similar, confirming the essential interchangability of the two approaches for structure matching — at least for complexes of the present type (see footnotes to Table 1).

## 4. Molecular mechanics results

X-ray structural data exist for $[Co(cyclen)(NO_2)_2]^+$ [36], $[Co(cyclen)CO_3]^+$ [37], $[Co(tren)(NO_2)_2]^+$ [25] and $[Co(tren)CO_3]^+$ [38]. These complexes appeared appropriate for study in the present context since structures incorporating both cyclen and tren are represented with and without an adjoining four-membered (carbonato) chelate ring. As mentioned earlier, the cyclen-complex assisted hydrolysis of BNPP is 58 times greater than the tren analogue [24].

The X-ray data show that the O–Co–O bond angles in $[Co(tren)CO_3]^+$ at 68.5° [38] and $[Co(cyclen)CO_3]^+$ at 68.4° [37] are much reduced relative to the corresponding $NO_2$–Co–$O_2N$ bond angles of $[Co(tren)(NO_2)_2]^+$ at 85.7° [25] and $[Co(cyclen)(NO_2)_2]^+$ at 84.5° [36]. Of particular relevance to the present study is the fact that the angle opposite the O–Co–O bond angle in $[Co(cyclen) CO_3]^+$ (103.1°) is 7.7° larger than the corresponding angle in $[Co(cyclen)(NO_2)_2]^+$ (95.4°). In contrast, the more rigid system $[Co(tren)CO_3]^+$ contains a bond angle of 87.9° opposite the O–Co–O angle — about the same as the corresponding angle in $[Co(tren)(NO_2)_2]^+$ (87.3°). The complexes of tren are more rigid because the presence of a bound apical nitrogen bridgehead coupled with the formation of only

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[1] Density functional electronic structure code written at James Cook University by K.R. Adam.

Table 1
Summary of molecular mechanics structural and steric energy

| Parameter | $[Co(cyclen(NO_2)_2]^+$ | $[Co(cyclen)CO_3]^+$ | $[Co(tren)(NO_2)_2]^+$ | $[Co(tren)CO_3]^+$ |
|---|---|---|---|---|
| Steric energy (kJ $mol^{-1}$) | 116 | 147 | 111 | 138 |
| R.M.S. deviation bonds (Å) | 0.024 | 0.039 | 0.026 | 0.027 |
| R.M.S. deviation angles (°) | 1.9 | 2.5 | 2.5 | 2.7 |
| R.M.S. deviation torsions (°) | 3.2 | 4.8 | 5.2 | 8.4 |
| R.M.S. deviation distances (Å) | 0.060 | 0.073 | 0.074 | 0.059 |
| Angle N–Co–N[a] | 98.3<br>(95.4)[b,c] | 103.6<br>(103.0)[b,d] | 88.7<br>(87.1)[b,e] | 88.6<br>(88.0)[b,f] |

[a] Angle defined by the amine nitrogens opposite the carbonato ligand.

[b] Bracketed value is the observed value in the corresponding X-ray structure (see text).

[c] The value obtained from the corresponding DFT minimisation was 99.0°.

[d] The value obtained from the corresponding DFT minimisation was 102.8°.

[e] The value obtained from the corresponding DFT minimisation was 86.1°.

[f] The value obtained from the corresponding DFT minimisation was 86.5°.

five-membered chelate rings results in 'tight' coordination of tren such that its degrees of freedom are substantially reduced; in contrast, when it coordinates in a *cis* fashion, the cyclen ligand is considerably less constrained.

Table 1 contains a summary of the important structural and energy terms from the molecular mechanics calculations while Figs. 1 and 2 illustrate the minimised structures of the $[Co(tren)(NO_2)_2]^+$, $[Co(tren)CO_3]^+$, $[Co(cyclen)(NO_2)_2]^+$ and $[Co(cyclen)CO_3]^+$.

Overall, our molecular mechanics calculations yielded structures that are in reasonable accord with the observed X-ray data for the above complexes of tren and cyclen. Moreover, the chemically significant structural differences mentioned earlier are reasonably reproduced; in particular, the calculated expansion of the N–Co–N angles opposite the coordinating anion(s) for the complex containing cyclen is 5.5°, while it is 0.1° for the corresponding complex of tren. The molecular mechanics calculations are clearly able to reproduce the steric accommodation of the four-membered ring in $[Co(cyclen)CO_3]^+$ through expansion of the N–Co–N angle opposite the O–Co–O chelate. Because of the stoichiometric differences between the complexes considered here, steric energies are not comparable between the various complexes so that no comment can be made concerning these values.

No corresponding X-ray structural data were available for the complexes of trpn and hence no direct comparison between X-ray and molecular mechanics structures was possible. The large number of conformational possibilities arising from the three (somewhat flexible) six-membered chelate rings formed by the trpn ligand on coordination to Co(III) led to difficulties in attempting to model such species in the

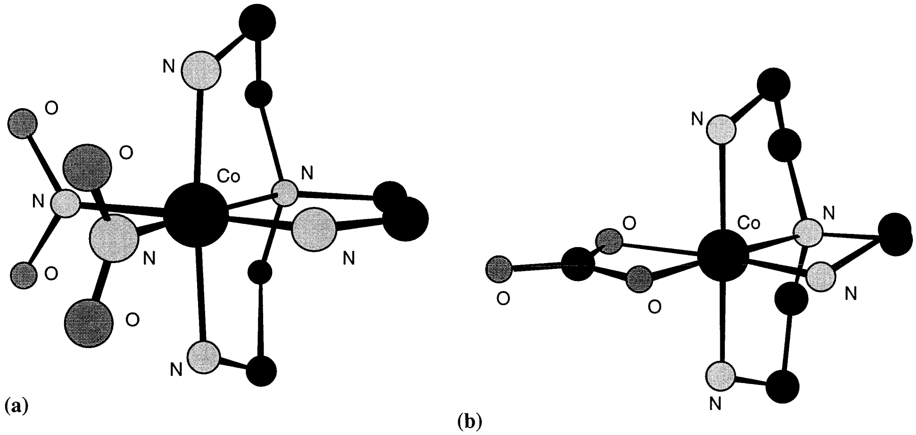

Fig. 1. The MM2 minimised structure of (a) $[Co(tren)(NO_2)_2]^+$ and (b) $[Co(tren)CO_3]^+$.

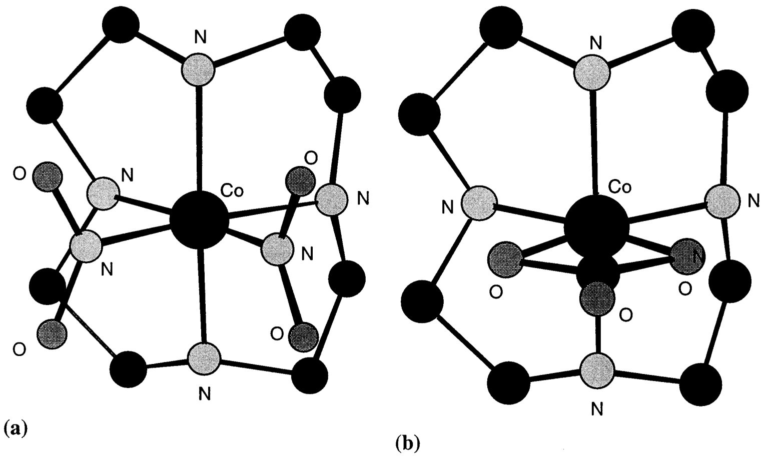

Fig. 2. The MM2 minimised structure of (a) $[Co(cyclen)(NO_2)_2]^+$ and (b) $[Co(cyclen)CO_3]^+$.

absence of comparable X-ray data. However, preliminary calculations on selected conformers of $[Co(trpn)(CO_3)]^+$ and $[Co(trpn)(NO_2)_2]^+$ indicate that the N–Co–N angle opposite the carbonato ligand in the former complex is again expected to show considerable expansion (perhaps, to around 107°) relative to the corresponding angle in the latter — again reflecting accommodation of the four-membered (carbonato) chelate ring in the coordination sphere of $[Co(trpn)(CO_3)]^+$.

## 5. Concluding remarks

Subject to the usual caution that needs to be exercised when applying molecular mechanics to the study of metal-containing species [12], it is clear that the modified

Allinger force field presented is applicable to a range of Co(III) complexes incorporating chelating amine ligands together with (monodentate) nitro or bidentate carbonato ligand species. Moreover, the results confirm that the molecular mechanics technique shows considerable potential as an aid in the design of synthetic phosphate diestersases exhibiting enhanced esterase-like activity.

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