stitution reaction and the influence of substituents on the molecule folding.

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Relationship Between X-ray Structure and Phosphodiesterase Activity of Co^{III} Complexes: Structure of Dinitro[tris(2-aminoethyl)amine]cobalt(III) Chloride

BY JIK CHIN* AND MARC DROUIN

Department of Chemistry, McGill University, Montreal, Canada, H3A 2K6

AND ANDRÉ G. MICHEL*

Laboratoire de chimie structurale, Département de chimie, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Québec, Canada, J1K 2R1

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Abstract. [$Co(NO_2)_2(C_6H_{18}N_4)$]Cl, M_r = 332·6, orthorhombic, *Pcmb*, a = 8·452 (6), b = 12·0735 (4), c = 12·1733 (8) Å, V = 1242·23 Å^3, D_x = 1·778 Mg m^{-3}, Z = 4, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·61 mm^{-1}, F(000) = 687·80, room temperature, final R = 0·024 for 749 reflections in the range 00·00 < 2θ < 47·90°. All of the *cis* N—Co—N bond angles in the parent compound are essentially the same as the corresponding angles in [(tren)Co(CO_3)]$^+$ [tren: tris(2-aminoethyl)amine]. In sharp contrast, one of the *cis* N—Co—N bond angles increases dramatically on going from [(cyclen)Co(NO_2)$_2$]$^+$ to [(cyclen)Co(CO_3)]$^+$ (cyclen: 1,4,7,11-tetraazacyclododecane). Relative reactivity of [(tren)Co(OH_2)(OH)]$^{2+}$ and [(cyclen)Co(OH_2)(OH)]$^{2+}$ in hydrolyzing phosphate diesters is explained in terms of the *cis* N—Co—N bond angle.

Introduction. Currently there is much interest in designing catalysts that hydrolyze the phosphate diester backbone of DNA (Dervan & Moser, 1987). We recently showed that *cis* aquahydroxo(tetraamine)Co^{III} complexes are highly efficient at hydrolyzing phosphate diesters (Chin & Zou, 1988). Furthermore, the reactivity of Co^{III} complexes is extremely sensitive to the tetraamine ligand structure (Chin, Banaszczyk, Jubian & Zou, 1989; Chin & Banaszczyk, 1989*a*,*b*). For example, the phosphate diester bond in (1) is hydrolyzed about 50 times more rapidly than that in (2). In order to find out why (1) is so much more reactive than (2), we determined the crystal structure of (2′) (see Fig. 1).

Experimental. [(tren)Co(NO_2)$_2$]Cl was prepared from [(tren)CoCl_2]Cl following the procedure described for the preparation of [(en)$_2$Co(NO_2)$_2$]Cl (Bernal, 1985). Anal. calc. for [Co($C_6H_{18}N_4$)(NO_2)$_2$]Cl: C 21·68, H 5·46, N 25·39%. Found: C 22·06, H 5·25, N 25·66%.

The X-ray diffraction was performed on an orange rectangular crystal, 0·20 × 0·20 × 0·25 mm; Enraf–Nonius CAD-4 diffractometer with graphite monochromator and Mo $K\alpha$ radiation. The cell dimen-

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* Authors to whom correspondence should be addressed.

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sions were obtained from 31 reflections with $40{\cdot}00 < 2\theta < 45{\cdot}00°$, *hkl* range: $h = 8$, $k = 12$, $l = 13$. The $\omega/2\theta$ scan mode was used with maximum 2θ of 47·9°. 3 standard reflections measured every 100 reflections; variation 2%. 851 reflections were measured [749 with $I_{\rm net} > 2{\cdot}5\sigma(I_{\rm net})$]. The structure was solved by direct methods and refined on F with *NRCVAX* (Gabe, Lee & LePage, 1985). The last least-squares cycles were calculated with 22 atoms, 94 parameters. Weights based on counting statistics were used. The final residuals for significant reflections were $R_f = 0{\cdot}024$, $wR = 0{\cdot}020$ and $S = 2{\cdot}272$; structure factors from *International Tables for X-ray Crystallography* (1974). All H atoms were calculated and refined isotropically. The secondary-extinction coefficient was refined and converged to 0·18 (2) (Larson, 1967; Zachariasen, 1963). The maximum shift/e.s.d. ratio was 0·131. In the last D map, the deepest hole was $-0{\cdot}35$ e Å^{-3} and the highest peak 0·26 e Å^{-3} both around C4. The high thermal parameters on C4 show a disordered atom because of the non-planarity of the five-membered ring. The Co, C3, C4, N1, N3, N6 and N5 atoms are in a crystallographic mirror and Cl on a 2 axis, all with a multiplicity of four. All other atoms are on a general position with a multiplicity of eight.

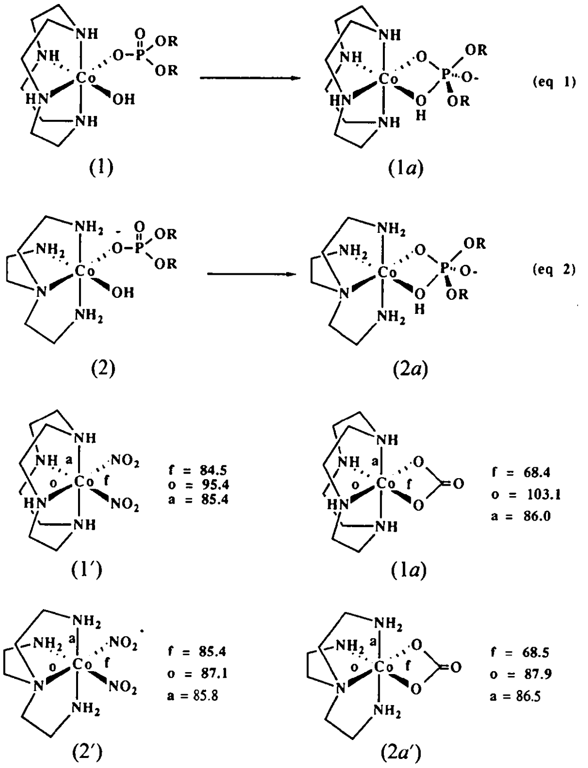

Fig. 1. Change in *cis* N—Co—N bond angles (°) with four-membered ring formation.

Fig. 2 shows the *ORTEP* diagram of [(tren)Co(NO$_2$)$_2$]$^+$. The final parameters and $B_{\rm eq}$ values for the cobalt complex are given in Table 1.* The Co atom is surrounded by six nitrogens. The Co—N bond lengths range from 1·963 (3) to 1·909 (3) Å (Table 2).

The *cis* N—Co—N bond angles included in the three five-membered rings are 85·82 (7)° for N1—Co—N2 and N1—Co—N4, and 87·14 (14)° for N1—Co—N3 respectively. Fig. 3 shows the packing diagram. Each of the primary amines is involved in two hydrogen bonds: N2 (and N4 by symmetry) with two different Cl (hydrogen bonds 1 and 4); and N3 with two Cl (hydrogen bonds 2 and 3). The Cl atom is intercalated in such a way as to form four hydrogen bonds with two different molecules of the cobalt complex.

Discussion. Cobalt complexes (1) and (2) are closely related structurally and electronically. Both are held rigidly in the *cis* form and cannot isomerize to the *trans* form (Iitaka, Shina & Kimura, 1974). The Lewis acidity of the two cobalt centers should be comparable since the basicities of the metal hydroxides in (1) and (2) are about the same (Chin, Banaszczyk, Jubian & Zou, 1989). Why then should

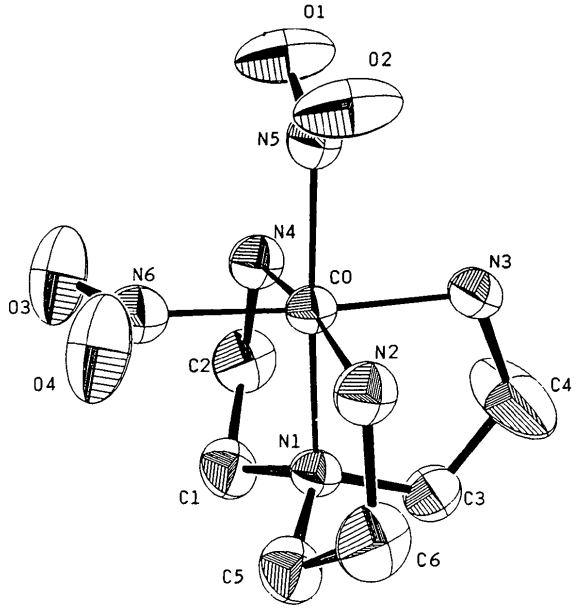

Fig.2. Thermal ellipsoid plot (50% probability level) and atomic labeling for [Co(tren)(NO$_2$)$_2$]$^+$.

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* Lists of structure factors, torsion angles, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52585 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final coordinates and B values for non*-H *atoms with e.s.d.'s in parentheses*

	x	*y*	*z*	B_{eq} (Å^2)
Co	0·27283 (6)	3/4	0·13253 (4)	1·56 (3)
Cl	0·96396 (13)	1/2	1/4	2·62 (5)
N1	0·2425 (4)	3/4	−0·02732 (25)	1·70 (16)
N3	0·0437 (4)	3/4	0·1455 (3)	1·95 (16)
N4	0·2772 (3)	0·58895 (18)	0·12036 (18)	2·14 (11)
N5	0·2923 (4)	3/4	0·2888 (3)	2·07 (17)
N6	0·5041 (4)	3/4	0·1316 (3)	2·31 (18)
C1	0·3186 (4)	0·6465 (3)	−0·06900 (23)	2·55 (14)
C2	0·2657 (4)	0·55327 (23)	0·00341 (24)	2·89 (15)
C3	0·0686 (5)	3/4	−0·0548 (4)	2·48 (22)
C4	−0·0333 (7)	3/4	0·0408 (4)	8·2 (5)
O1	0·2989 (3)	0·66185 (17)	0·33969 (15)	3·82 (12)
O3	0·5787 (3)	0·66221 (19)	0·13638 (19)	4·19 (12)

Table 2. *Intramolecular bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co—N(1)	1·963 (3)	N(3)—C(4)	1·431 (6)
Co—N(2)	1·9504 (21)	N(4)—C(2)	1·491 (4)
Co—N(3)	1·943 (4)	N(5)—O(1)	1·233 (3)
Co—N(4)	1·9504 (21)	N(5)—O(2)	1·233 (3)
Co—N(5)	1·909 (3)	N(6)—O(3)	1·235 (3)
Co—N(6)	1·955 (4)	N(6)—O(4)	1·235 (3)
N(1)—C(1)	1·495 (3)	C(1)—C(2)	1·498 (4)
N(1)—C(5)	1·495 (3)	C(3)—C(4)	1·447 (7)
N(1)—C(3)	1·508 (6)		
N(1)—Co—N(3)	87·14 (14)	Co—N(1)—C(3)	110·30 (24)
N(1)—Co—N(4)	85·82 (7)	C(1)—N(1)—C(5)	113·5 (3)
N(1)—Co—N(2)	85·82 (7)	C(1)—N(1)—C(3)	110·16 (19)
N(1)—Co—N(5)	177·45 (14)	C(5)—N(1)—C(3)	110·16 (19)
N(1)—Co—N(6)	97·17 (14)	Co—N(3)—C(4)	112·4 (3)
N(3)—Co—N(4)	91·44 (7)	Co—N(4)—C(2)	111·07 (16)
N(3)—Co—N(2)	91·44 (7)	Co—N(5)—O(1)	120·30 (16)
N(3)—Co—N(5)	90·31 (14)	Co—N(5)—O(2)	120·30 (16)
N(3)—Co—N(6)	175·69 (15)	O(1)—N(5)—O(2)	119·4 (3)
N(4)—Co—N(2)	171·01 (10)	Co—N(6)—O(3)	120·70 (18)
N(4)—Co—N(5)	94·25 (7)	Co—N(6)—O(4)	120·70 (18)
N(4)—Co—N(6)	88·88 (7)	O(3)—N(6)—O(4)	118·3 (3)
N(2)—Co—N(5)	94·25 (7)	N(1)—C(1)—C(2)	107·45 (23)
N(2)—CO—N(6)	88·88 (7)	N(4)—C(2)—C(1)	108·98 (22)
N(5)—Co—N(6)	85·38 (15)	N(1)—C(3)—C(4)	113·7 (4)
Co—N(1)—C(1)	106·28 (17)	N(3)—C)4)—C(3)	116·4 (4)
Co—N(1)—C(5)	106·28 (17)		

The following atoms are the symmetry equivalents

N(2) and N(4)	*x*	1·500 − *y*	*z*
C(5) and C(1)	*x*	1·500 − *y*	*z*
C(6) and C(2)	*x*	1·500 − *y*	*z*
O(2) and O(1)	*x*	1·500 − *y*	*z*
O(4) and O(3)	*x*	1·500 − *y*	*z*

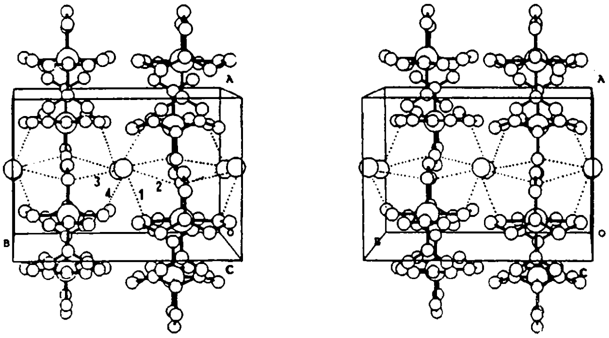

Fig. 3. Stereoview of the unit-cell content of $[Co(tren)(NO_2)_2]^+$ with intermolecular hydrogen bonds represented in dotted lines.

the reactivity of the phosphate diester bond in (1) and (2) be so sensitive to the tetraamine ligand structure? Hydrolysis of (1) and (2) involves the formation of a four-membered ring translation state or intermediate (equations 1 and 2). This should result in considerable distortion of the octahedral complex. For example, X-ray data show that (1*a*′) (Schlemper, Sen Gupta & Dasgupta, 1983) and (2*a*′) (Leohlin & Fleischer, 1976) are distorted compared to (1′) and (2′) respectively. The O—Co—O bond angles (*f*, Fig. 1) of (1*a*′) (68·4°) and (2*a*′) (68·5°) are significantly less than the corresponding (*f*) angles of (1′) (84·5°) (Iitaka, Shina & Kimura, 1974) and (2′) (85·4°). There is one outstanding difference between the Co(cyclen) system and the Co(tren) system. On going from structure (1′) to (1*a*′) all of the *cis* N—Co—N bond angles remain essentially the same except the angle opposite (*o*) the four-membered ring which increases dramatically (7·7°). In sharp contrast, on going from (2′) to (2*a*′), all of the *cis* N—Co—N bond angles including the opposite angle (*o*) remain essentially the same. The opposite angle (*o*) in (2*a*′) is locked into a five-membered ring and cannot be expanded significantly.

The Co(cyclen) system and the Co(tren) system are particularly well suited for comparison. Both (1*a*′) and (2*a*′) have several N—Co—N bond angles that are locked into five-membered rings. In (1*a*′) it is the N—Co—N bond angle that is *opposite* (*o*) the O—Co—O bond angle that is not locked into a five-membered ring. In (2*a*′) two N—Co—N bond angles that are *adjacent* (*a*) to the O—Co—O bond angle are free. The four-membered ring formation results in the increase in the N—Co—N bond angles opposite the four-membered ring but does not affect the N—Co—N bond angle adjacent to it. The four-membered ring is stabilized by increasing the opposite N—Co—N bond angle but is not affected significantly by the adjacent N—Co—N bond angles.

Clearly structures (1*a*′) and (2*a*′) are not the same as structures (1*a*) and (2*a*) respectively. However, the O—Co—O bond angles in (1*a*) and (2) should also be considerably less than the 90° angle found in regular octahedral complexes for the following reasons. In a totally strain-free system, the O—Co—O, Co—O—P, O—P—O and P—O—Co bond angles in (1*a*) or (2*a*) should add up to 399° (90 + 109·5 + 90 + 109·5). In any four-membered ring, the sum of the angles must be less than or equal to 360°. Therefore, each of the four angles in the four-membered ring [(1*a*) or (2*a*)] must be compressed compared to the strain-free bond angles. In particular, the O—Co—O bond angles in (1*a*) and (2*a*) should be less than 90°.

It is well known that in enzymic systems, subtle changes in the structure of the active center can greatly influence the activity of the enzyme. We have shown that subtle changes in the tetraamine ligand structure causes a change in the *cis* N—Co—N bond angle and a dramatic change in the reactivity of the cobalt complex. Knowledge of such detailed structure–reactivity relationship is valuable since it can give insights into the rational design of highly reactive cobalt complexes.

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Structure of 1-Methyl-1*H*-imidazole-5-ethanamine Dihydrochloride

By Marek L. Główka, Zdzisław Gałdecki and Iwona Iwanicka

Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90-924 *Łódź, Poland*

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Abstract. 4-(2-Ammonioethyl)-1-methyl-3H^+-imidazolium chloride, $C_6H_{13}N_3^{2+}.2Cl^-$, $M_r = 198{\cdot}10$, monoclinic, $P2_1/n$, $a = 4{\cdot}60\,(1)$, $b = 13{\cdot}57\,(1)$, $c = 15{\cdot}43\,(2)$ Å, $\beta = 98{\cdot}37\,(3)°$, $V = 952{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}381$, $D_m = 1{\cdot}38$ Mg m^{-3}, $F(000) = 416$, $T = 293$ K, Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å), $\mu = 6{\cdot}29$ mm^{-1}, $R = 0{\cdot}030$ for 1484 reflections used in the refinement. Diprotonated methylhistamine molecules are hydrogen bonded through chloride ions. The ethylamine chain is in a *trans* conformation and the plane defined by three non-H atoms of the chain is perpendicular to the plane of the imidazole ring.

Introduction. Ganellin's works on conformation and activity of histamine and methylhistamines have shown that the *trans* conformation of the ethylamine chain dominates in aqueous solution for all protonated forms and that *N*-methylation has little influence on the chain conformation (Ganellin, 1973; Ganellin, Pepper, Port & Richards, 1973; Ganellin, Port & Richards, 1973). However, *pros*-methylation seems to be important for the orientation of the ethylamine chain. Thus we undertook this study as a continuation of the program on structures of histamines and their complexes (Główka, Gałdecki, Kazimierczak & Maśliński, 1980; Główka & Gilli, 1989).

Experimental. The crystals of the compound were recrystallized from 2-propanol. D_m by flotation. The intensity data to $\theta_{\max} = 25°$ were obtained from a crystal of size $0{\cdot}44 \times 0{\cdot}38 \times 0{\cdot}15$ mm by $\omega/2\theta$ scan technique on a CAD-4 diffractometer. Cell constants from setting angles of 25 reflections with $9 < \theta < 15°$. 3 standard reflections, measured every 100 reflections; 2% variation. $-5 \le h \le 5$; $0 \le k \le 15$; $0 \le l \le 18$. From the 1860 reflections measured, 1637 had $I > 3\sigma(I)$. Absorption was neglected. The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1986) and H-atom positions were found from difference Fourier maps. The final agreement factors of 0·030 (R) and 0·041 (wR) were obtained after full-matrix least-squares refinement on F based on 1484 intensities with $F_o > 3\sigma(F_o)$ (non-H atoms with anisotropic and H atoms with isotropic thermal parameters). The final weighting scheme used was $w = k/[\sigma^2(F_o) + dF_o^2]$, where k and d were 0·382 and 0·0079, respectively. $(\Delta/\sigma)_{\max} = 0{\cdot}08$. Max. and min.

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