A Structural and Isotopic NO_2^- Exchange Rate Comparison of *trans*-$[Co(ao–H–ao)(NO_2)_2]$ and *cis*-$[Co(Hao)_2(NO_2)_2]NO_3$[†]

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The *X*-ray crystal structures of two non-isomeric (α-amineoxime)dinitrocobalt(III) complexes, *trans*-$[Co(ao–H–ao)(NO_2)_2]$ and *cis*-$[Co(Hao)_2(NO_2)_2]NO_3$ (Hao = 3-amino-3-methyl-2-butanone oxime), have been refined to conventional *R* values of 0.034 (*trans*) and 0.032 (*cis*). The neutral *trans* complex crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 6.786(3), b = 11.553(1), and c = 20.908(2) Å. The *cis* nitrate salt crystallizes in the monoclinic space group $P2_1/n$ with a = 8.160(3), b = 17.250(3), c = 13.745(2) Å, and β = 104.77(2)°. Only the former species has an intramolecular hydrogen bond, and this is, to our knowledge, the first comparison of non-isomeric (due to charge) *cis–trans* complexes. The differences in the organic ligand and nitro bond distances and angles are discussed. The structural, u.v.–visible, and n.m.r. spectroscopic parameters are presented. The bond distances to the nitro groups are compared with their isotopic exchange lability in aqueous solution. It is concluded that the kinetic lability of the nitro ligands, as measured by ^{15}N isotopic exchange rates is not directly related to the metal–nitrogen bond distance in the solid state.

With cobalt(III) or nickel(II), where the solution and solid geometries can more easily be determined than with many other metal ions, the α-amineoxime complexes almost universally give complexes with a planar ligand arrangement and with the oxime groups *cis*; this results in a strong internal hydrogen bond.[1] From the evidence available, this also appears to be true with copper(II),[2] palladium(II),[3] platinum(II),[4] and rhodium(III).[5] The dominance of the hydrogen bond is also evidenced in the dimethylglyoxime (H_2dmg) complexes of the same metal ions where all the atoms of the ligands are in a single plane. So strong is this tendency that H_2dmg structures in which the ligands are not coplanar are seldom considered. An exception to this appears to be the tris(H_2dmg) complex of cobalt(III), where intramolecular hydrogen bonds are not possible.[6] We have determined the structure of $[Co(H_2dmg)_3]_2[PtCl_6]_3$, which will be published in the near future.

Some years ago we reported the preparation of *cis*-$[Co(Hao)_2(NO_2)_2]NO_3$[7] (Hao = 3-amino-3-methyl-2-butanone oxime) but the evidence for the *cis* configuration was limited, being based solely on the fact that neutralization did not produce the known *trans*-$[Co(ao–H–ao)(NO_2)_2]$. An alternative explanation could have been that it was the *trans*-dinitro-*trans*-bis(3-amino-3-methyl-2-butanone oxime) complex which also would not have the internal hydrogen bond.

In this study we present the preparations and *X*-ray crystal structures of the two title dinitro complexes and make structural comparisons. The preparative differences suggest a mechanistic interpretation which may lead to the preparation of the analogous *cis*-dimethylglyoxime cobalt(III) complexes.

A second feature of interest is the unsymmetrical positions occupied by the unidentate ligands in both structures. This should result in different $Co–NO_2$ bond lengths and unequal rates of isotopic $^{15}NO_2^-$ substitution such as observed in the analogous *trans*-$[Co(pnao)(NO_2)_2]$ [Hpnao = 3,3′-(1,3-diaminopropane)-*N*,*N*′-bis(3-methyl-2-butanone oxime)][8] complex. As will be shown, the complexes are not isomeric and the kinetic differences observed are largely due to the charge difference of the complex ions in solution. The u.v.–visible and n.m.r. spectral characteristics are described and the rates of interconversions are compared for these complexes.

Experimental

Crystal Data.—A. For trans-$[Co(ao–H–ao)(NO_2)_2]$. A crystal of approximate dimensions 0.20 × 0.14 × 0.12 mm was aligned automatically on the basis of 25 centred reflections arbitrarily selected by an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation (λ = 0.7107 Å). From systematic absences, the least-squares unit cell is orthorhombic, space group $P2_12_12_1$, with a = 6.786(3), b = 11.553(1), c = 20.908(2) Å, Z = 4, D_c = 1.549, D_m = 1.55(1) g cm^{-3}, $F(000)$ = 800, U = 1 639.2(1.0) $Å^3$; $C_{10}H_{23}CoN_6O_6$, M = 382.26. A set of three-dimensional intensity data was collected at 21 °C, using Mo-K_α radiation from a graphite monochromator, and the θ–2θ step scan technique. Data were collected for 2θ from 3 to 50° for hkl and $\bar{h}\bar{k}\bar{l}$ and from 50 to 55° for $\bar{h}\bar{k}\bar{l}$. The intensities of 3 891 reflections were measured with variable scan speeds to maintain counting statistics to 2.0% up to a maximum scan time of 120 s. 3 357 Reflections had $F^2 > 2\sigma(F^2)$, and these gave 2 923 independent observations (277 parameters). Standard reflections were measured after every 6 000 s of *X*-ray exposure, showing no decomposition over the period of measurement. Crystal orientation was maintained by checking the centring of three reflections after the measurement of each 200 reflections. Empirical absorption correction factors from psi scans were applied and ranged from 0.77 to 1.0, μ = 11.3 cm^{-1}. $R(F) = \Sigma||F_o| - |F_c||/\Sigma F_o = 0.034$, $R'(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^{\,2}]^{\frac{1}{2}} = 0.041$. Maximum shift to error ratio in last cycle was 0.08.

B. For cis-$[Co(Hao)_2(NO_2)_2]NO_3$. A crystal of approximate dimensions 0.15 × 0.15 × 0.10 mm was used, with the same radiation and diffractometer, and found to have a monoclinic unit cell, space group $P2_1/n$, with a = 8.160(3), b = 17.250(3), c = 13.745(2) Å, β = 104.77(16)°, Z = 4, D_c = 1.581, D_m = 1.59(1) g cm^{-3}, $F(000)$ = 928, U = 1 870.9(1.4) $Å^3$;

[†] *trans*-{Hydrogenbis[3-amino-3-methyl-2-butanone oximato(1 −)]}-dinitrocobalt(III) and *cis*-bis(3-amino-3-methyl-2-butanone oxime)-dinitrocobalt(III) nitrate.

Supplementary data available (No. SUP 56528, 12 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Co	0.022 65(5)	0.069 01(3)	0.213 69(3)
O(1)	−0.296 2(3)	0.053 0(1)	0.059 3(2)
O(2)	−0.075 9(3)	0.191 7(1)	0.329 7(2)
O(3)	0.068 1(4)	−0.049 5(2)	0.094 0(2)
O(4)	0.261 1(3)	0.035 0(2)	0.107 1(2)
O(5)	0.250 5(3)	−0.015 8(2)	0.335 3(2)
O(6)	0.285 0(3)	0.186 3(2)	0.374 0(2)
O(7)	0.178 9(3)	0.212 5(2)	0.774 6(2)
O(8)	0.010 8(4)	0.304 3(2)	0.707 9(3)
O(9)	−0.084 8(4)	0.189 6(2)	0.715 7(3)
N(1)	−0.098 9(3)	0.113 8(2)	0.302 3(2)
N(2)	−0.152 3(3)	0.099 3(2)	0.097 0(2)
N(3)	−0.095 3(3)	−0.022 8(2)	0.240 0(2)
N(4)	0.118 6(3)	0.166 9(2)	0.185 3(2)
N(5)	0.132 6(3)	0.012 1(2)	0.129 8(2)
N(6)	0.208 7(3)	0.050 1(2)	0.327 7(2)
N(7)	0.032 6(4)	0.235 8(2)	0.731 4(2)
C(1)	−0.193 3(4)	0.072 1(2)	0.342 1(2)
C(2)	−0.143 1(4)	0.163 7(2)	0.053 3(3)
C(3)	−0.206 6(4)	−0.012 3(2)	0.310 9(3)
C(4)	0.020 3(4)	0.207 8(2)	0.092 3(3)
C(5)	−0.288 6(5)	0.103 1(2)	0.412 9(5)
C(6)	−0.276 2(5)	0.193 1(2)	−0.033 9(3)
C(7)	−0.389 1(5)	−0.032 1(2)	0.285 5(3)
C(8)	−0.140 5(5)	−0.063 8(2)	0.402 8(3)
C(9)	−0.012 4(5)	0.291 3(2)	0.118 3(3)
C(10)	0.119 8(5)	0.206 3(2)	0.012 2(3)

Atom	x	y	z
Co	−0.454 78(6)	0.441 39(4)	0.071 85(2)
O(1)	−0.097 4(3)	0.420 3(3)	0.141 1(1)
O(2)	−0.070 0(3)	0.517 0(2)	0.038 6(1)
O(3)	−0.694 6(4)	0.612 8(2)	0.117 9(1)
O(4)	−0.393 3(4)	0.649 2(2)	0.135 0(1)
O(5)	−0.368 4(5)	0.205 3(2)	0.061 1(1)
O(6)	−0.359 1(4)	0.290 0(2)	−0.028 2(1)
N(1)	−0.291 0(4)	0.398 7(2)	0.141 4(1)
N(2)	−0.260 0(4)	0.513 8(2)	0.020 4(1)
N(3)	−0.655 7(4)	0.364 6(2)	0.122 7(1)
N(4)	−0.626 7(4)	0.483 2(2)	0.000 3(1)
N(5)	−0.519 8(4)	0.585 9(2)	0.113 2(1)
N(6)	−0.386 5(4)	0.294 8(2)	0.030 0(1)
C(1)	−0.367 3(5)	0.341 3(3)	0.188 0(2)
C(2)	−0.305 9(4)	0.549 1(3)	−0.035 3(1)
C(3)	−0.585 1(5)	0.323 7(3)	0.187 2(1)
C(4)	−0.524 0(4)	0.551 1(3)	−0.050 4(1)
C(5)	−0.243 7(6)	0.294 2(5)	0.241 1(2)
C(6)	−0.158 1(5)	0.588 6(3)	−0.082 0(2)
C(7)	−0.640 3(7)	0.197 4(3)	0.196 3(2)
C(8)	−0.677 5(6)	0.398 2(4)	0.239 2(2)
C(9)	−0.567 7(6)	0.495 8(4)	−0.116 0(2)
C(10)	−0.594 7(6)	0.676 5(3)	−0.048 5(2)
H(00)	−0.078(6)	0.463(3)	0.091(2)

$C_{10}H_{24}CoN_7O_9$, $M = 445.28$. 3 090 Reflection intensities were measured (2 518 independent), no decomposition was observed, and crystal orientation was checked every 200 reflections. Empirical absorption effects were small and corrections were not made ($\mu = 10.2$ cm^{-1}). After averaging equivalent reflections and retaining those having $F^2 > 1.5\sigma(F^2)$, 1 995 observations remained which were used to solve the structure (316 parameters). $R(F) = 0.032$, $R'(F) = 0.040$. Maximum shift to error ratio 0.11.

Preparation of Complexes.—*trans*-[Co(ao–H–ao)$(NO_2)_2$]. This was prepared as previously described[9] from [Co(ao–H–ao)Cl_2] and NO_2^- in slightly acidic media. Recrystallization was from methanol.

cis-[Co$(Hao)_2(NO_2)_2$]NO_3. The reaction of *trans*-[Co(ao–H–ao)Cl_2] with excess 1.0 mol dm^{-3} NaOH solution at 0 °C gave a solution of the *cis*-dihydroxy complex(es).* After neutralization with acetic acid to pH 5 the solution was treated with the theoretical amount of $NaNO_2$ and allowed to sit for 3 h. A small amount of the *trans*-dinitro complex was removed by filtration and the clear solution made 1 mol dm^{-3} in HNO_3 and saturated with $NaNO_3$. *cis*-[Co$(Hao)_2(NO_2)_2$]NO_3 was collected and recrystallized by cooling of a concentrated solution of 1 mol dm^{-3} in HNO_3.

Both complexes are stable, for short periods of time (hours), with respect to substitution in water and in dilute acid, and do not isomerize appreciably *in the presence of excess nitrite* over a period of a few hours at room temperature. However in the absence of excess NO_2^- the *cis* complex partially converts to *cis*-[Co$(Hao)_2(NO_2)(OH_2)$]$^{2+}$ with a half-life of *ca.* 4 h and then other products form from it. It has been shown by h.p.l.c.[10] that many products are formed including the *trans*-nitroaqua, two other geometrical forms of *cis*-dinitro, and the *trans*-dinitro complex. Ultimately at least 95% becomes *trans*-[Co(ao–H–ao)$(NO_2)_2$] which is the thermodynamically stable state. Only the *cis* isomer is acidic in solution due to the reversible ionization of an oxime hydrogen. The measured acidity constants, pK_1 and pK_2, are 2.6 and 4.4 respectively at 25 °C. In the *cis* isomer an intramolecular hydrogen bond is not formed.

Physical Studies.—Isotopic ^{15}N exchange studies on the *cis*-dinitro complex were conducted as previously described[11] for *trans*-[Co(ao–H–ao)$(NO_2)_2$] with the following modifications. Free NO_2^- in the aliquots was removed by reaction with excess sulphamic acid at 0 °C and the *cis*-[Co$(Hao)_2(NO_2)_2$][BPh_4] precipitated and purified. Treatment of this salt with excess warm 0.1 mol dm^{-3} NaOH gave free NO_2^- which was reacted with N_3^- in a vacuum apparatus at pH 3 to give N_2O. After chemical and physical purification the N_2O was analysed for ^{15}N content [mass ratio 45/(44 + 46)] on a Nuclide RMS16 mass spectrometer and compared with the same ratio for a standard N_2O sample.

Studies on the rates of aquation and isomerization were carried out by separation of complex species at pH 3.9 utilizing reverse-phase liquid chromatography (r.p.l.c.), a 30 cm C-18 column, u.v. detector and 5% methanol–water solution with heptanesulphonic acid as an ion-pairing agent.

Both X-ray structures were solved by conventional Patterson and Fourier methods. The full-matrix least-squares refinement minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma^2(F_o^2) = \sigma_c^2 + (0.03F_o^2)^2$. Atomic scattering factors were taken from ref. 12 and included anomalous scattering contributions. Hydrogen atoms were located from difference-Fourier maps and were isotopically refined with a fixed temperature factor of 5.0. The maximum shift/error on the last cycle was less than 0.20 in both cases. The final positional parameters for the non-hydrogen atoms are given in Table 1.

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* Hydrolysis of *trans*-dichloro complexes in strong base often gives inversion and the major products are the *cis*-isomers. In this case, under the conditions used, approximately 80% inversion takes place with inversion giving only one of the *cis*-isomers.

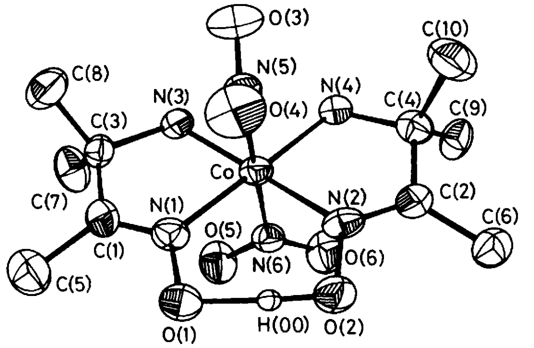

Figure 1. An ORTEP drawing of *trans*-[Co(ao–H–ao)$(NO_2)_2$] with the atom numbering system

Table 2. Bond distances (Å) with estimated standard deviations in parentheses

	cis[a]	*trans*[b]	*trans*-[Co(pnao)$(NO_2)_2$]
Co–N(1)	1.928(3)	1.896(3)	1.897(3)
Co–N(2)	1.918(3)	1.899(3)	1.904(3)
Co–N(3)	1.934(3)	1.934(3)	1.975(3)
Co–N(4)	1.942(3)	1.957(3)	1.979(3)
Co–N(5)	1.904(3)	1.932(3)	1.937(3)
Co–N(6)	1.911(3)	1.962(3)	1.984(3)
O(1)–N(1)	1.404(4)	1.337(3)	1.359(3)
O(2)–N(2)	1.396(3)	1.345(3)	1.347(3)
O(3)–N(5)	1.231(4)	1.230(4)	1.232(3)
O(1)–O(2)		2.423(3)	2.432(3)
N(4)–C(4)	1.501(5)	1.492(4)	1.521(3)
C(1)–C(3)	1.513(5)	1.492(5)	1.514(4)
C(1)–C(5)	1.491(5)	1.494(6)	1.494(4)
C(2)–C(4)	1.509(5)	1.513(5)	1.507(4)
C(2)–C(6)	1.487(6)	1.472(5)	1.537(4)
C(3)–C(7)	1.519(5)	1.519(5)	1.532(4)
C(3)–C(8)	1.526(5)	1.521(5)	1.537(4)
C(4)–C(9)	1.524(5)	1.542(5)	1.527(5)
C(4)–C(10)	1.525(5)	1.526(5)	1.534(4)
O(4)–N(5)	1.223(4)	1.216(4)	1.234(3)
O(5)–N(6)	1.220(4)	1.228(3)	1.250(3)
O(6)–N(6)	1.236(4)	1.231(3)	1.217(3)
O(7)–N(7)	1.256(4)		
O(8)–N(7)	1.227(4)		
O(9)–N(7)	1.222(4)		
N(1)–C(1)	1.274(4)	1.287(4)	1.276(3)
N(2)–C(2)	1.274(4)	1.272(4)	1.276(3)
N(3)–C(3)	1.502(5)	1.508(4)	1.523(3)
O(1)–H(1)	0.80(4)	1.17(4)	1.19
O(2)–H(2)	0.87(3)	1.26(4)	1.26

[a] *cis*-[Co$(Hao)_2(NO_2)_2$]NO_3. [b] *trans*-[Co(ao–H–ao)$(NO_2)_2$].

Table 3. Bond angles (°) with estimated standard deviations in parentheses

	cis[a]	*trans*[b]	*trans*-[Co(pnao)$(NO_2)_2$]
N(1)–Co–N(2)	91.5(1)	98.1(1)	98.6(1)
N(1)–Co–N(3)	94.6(1)	82.7(1)	82.0(1)
N(1)–Co–N(4)	81.2(1)	179.1(1)	176.0(1)
N(1)–Co–N(5)	89.9(1)	90.9(1)	88.4(1)
N(1)–Co–N(6)	173.4(1)	88.8(1)	87.7(1)
N(2)–Co–N(3)	81.3(1)	178.5(1)	177.7(1)
N(2)–Co–N(4)	94.5(1)	82.7(1)	82.2(1)
N(2)–Co–N(5)	172.7(1)	90.9(1)	88.0(1)
N(2)–Co–N(5)	88.8(1)	87.9(1)	89.0(1)
N(3)–Co–N(4)	174.0(1)	96.5(1)	97.1(1)
N(3)–Co–N(5)	91.5(1)	89.4(1)	94.1(1)
N(3)–Co–N(6)	92.0(1)	90.9(1)	
N(4)–Co–N(5)	92.9(1)	89.6(1)	95.5(1)
N(4)–Co–N(6)	92.1(1)	90.7(1)	88.4(1)
N(5)–Co–N(6)	90.6(1)	179.6(1)	174.8(1)
O(1)–N(1)–C(2)	117.8(3)	119.7(3)	119.2(2)
O(2)–N(2)–C(1)	118.8(3)	119.1(3)	119.3(2)
O(3)–N(5)–O(4)	118.6(3)	120.0(3)	118.4(2)
O(5)–N(6)–O(6)	120.5(3)	118.1(3)	119.4(2)
O(7)–N(7)–O(8)	119.3(4)		
O(7)–N(7)–O(9)	118.9(4)		
O(8)–N(7)–O(9)	121.8(4)		
N(1)–C(1)–C(3)	115.3(3)	117.5(3)	116.2(3)
N(1)–C(1)–C(5)	123.5(3)	121.6(4)	123.1(2)
C(3)–C(1)–C(5)	121.2(3)	121.0(3)	120.7(2)
N(2)–C(2)–C(4)	115.1(3)	115.9(3)	117.2(2)
N(2)–C(2)–C(6)	124.0(4)	122.6(3)	122.2(2)
C(4)–C(2)–C(6)	120.8(4)	121.5(3)	120.6(3)
N(3)–C(3)–C(1)	106.8(3)	106.4(3)	106.5(2)
N(3)–C(3)–C(7)	110.3(3)	109.5(3)	107.6(2)
N(3)–C(3)–C(8)	108.8(3)	109.3(3)	112.6(2)
C(1)–C(3)–C(7)	110.0(3)	112.0(3)	110.4(3)
C(1)–C(3)–C(8)	109.9(3)	108.9(3)	108.4(2)
C(7)–C(3)–C(8)	111.0(3)	110.7(4)	111.3(3)
N(4)–C(4)–C(2)	107.3(3)	107.4(3)	106.2(2)
N(4)–C(4)–C(9)	109.4(3)	108.9(3)	112.7(2)
N(4)–C(4)–C(10)	109.8(3)	109.5(3)	108.0(2)
C(2)–C(4)–C(9)	111.6(3)	111.6(3)	108.8(2)
C(2)–C(4)–C(10)	108.6(3)	108.6(3)	111.0(2)
C(9)–C(4)–C(10)	110.1(3)	110.9(4)	110.1(3)
O(1)–H(00)–O(2)		174(4)	168

[a] *cis*-[Co$(Hao)_2(NO_2)_2$]NO_3. [b] *trans*-[Co(ao–H–ao)$(NO_2)_2$].

Results

The structure of *trans*-[Co(ao–H–ao)$(NO_2)_2$] consists of discrete neutral molecules with the cobalt(III) atom in a slightly distorted octahedral configuration (Figure 1). The nitro groups are indeed *trans* and the amineoxime ligands *cis*, with a strong intramolecular hydrogen bond between the oxime oxygens. The nitro groups are dissimilar due to the non-planarity of the organic ligands at the sp^3 ring carbons [C(3) and C(4)]. The two $-NO_2$ planes have a dihedral angle of nearly 90°. Selected bond distances and bond angles are given in Tables 2 and 3 respectively.

The structure of *cis*-[Co$(Hao)_2(NO_2)_2$]NO_3 consists of discrete cobalt complex unipositive ions and NO_3^- ions with the cobalt atom in a nearly octahedral configuration (Figure 2). The NO_2^- groups are *cis* to each other and are *trans* to the oxime-nitrogen atoms of the organic ligands. They are in chemically equivalent but crystallographically non-equivalent positions. The Hao ligands are also in chemically equivalent positions with the amine groups *trans* to each other. Thus, of the several geometric structures possible, one of the most symmetrical is obtained. Only a few crystals were studied, however, and significant quantities of the other isomers could have been present. This is unlikely, however, since the bulk substance has been shown [10] to be a single compound ($\pm 1\%$) by analysis using r.p.l.c. Selected bond distances and angles for *cis*-[Co$(Hao)_2(NO_2)_2$]NO_3 are given in Tables 2 and 3 respectively.

The *trans*-dinitro ao–H–ao complex has a similar structure to that found in *trans*-[Co(pnao)$(NO_2)_2$].[13] The interesting difference lies in the Co–N(nitro) distances. In the pnao analogue the Co–N(nitro) distances are 1.984(3) and 1.937(3) Å while those in the ao–H–ao analogue reported here are 1.962(3) and 1.932(3) Å. In the former case we felt that the differences in the nitro distances within the molecule were caused by electronic, not steric, factors. The effect is also present in the *trans*-dinitro ao–H–ao complex but is about two-thirds the

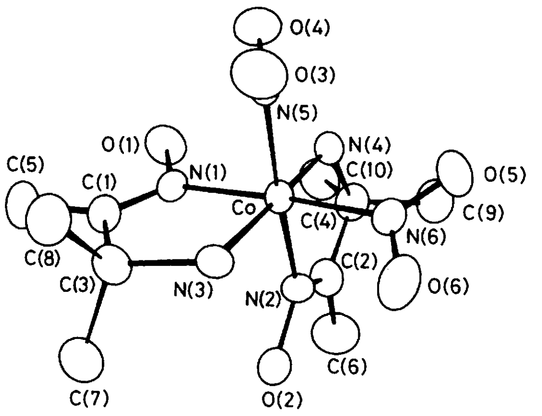

Figure 2. An ORTEP drawing of *cis*-$[Co(Hao)_2(NO_2)_2]^+$ with the atom numbering system

Table 4. N.m.r. assignments[a]

^{1}H			^{13}C		
Assignment[b]	*trans*[c]	*cis*[d]	Assignment	*trans*[c]	*cis*[d]
C^5,C^6[d]	2.01 (6)	1.38 (6)	C^1,C^2	160.597 (2)	182.340 (2)
C^7,C^9	1.31 (12)	2.09 (6)	C^3,C^4	61.078 (2)	62.275 (2)
C^8,C^{10}		1.58(6)	C^7,C^9 C^8,C^{10}	26.031 (4)	26.49 (2) 25.477 (2)
N^3,N^4	5.18 (4)	5.11 (1)	C^5,C^6	13.261 (2)	14.665 (2)
		5.24 (1)			
		5.44 (1)			
		5.57 (1)			
OHO	19.1 (1)				

[a] In p.p.m. downfield from $SiMe_4$ (C and H); CD_3Cl solvent; relative intensities in parentheses. [b] Protons on these carbons (see Figures 1 and 2). [c] *trans*-$[Co(ao–H–ao)(NO_2)_2]$. [d] *cis*-$[Co(Hao)_2(NO_2)_2]NO_3$.

magnitude. The long Co–N distance in both structures is associated with the nitro group which has its ONO plane nearly parallel to the line connecting O–H–O. These results suggest that the Hao and ao–H–ao ligands are less 'five-co-ordinate-producing' than is pnao or that the unsymmetrical distribution of the methyl groups around the sp^3 carbon in the five-membered chelate ring dictates the asymmetry of the 5 and 6 positions about Co^{III}. There is some tendency toward five co-ordination and the nitro groups in the *trans*-dinitro ao–H–ao complex, in the solid state at least, should be chemically different as was found in solution for the pnao complex.[13] In most other respects the two *trans*-dinitro complexes have almost identical bond distances and angles (Tables 2 and 3). The numbering system used in the previous paper has been modified for these tables to correspond with that used in the title complexes.

Distances and Angles involving the Amineoxime Ligands.— The bond distances and angles within and involving the amineoxime ligand are remarkably constant for the *cis*-Hao and *trans*-ao–H–ao complexes and they are also very similar to those in the *trans*-pnao complex.[13] The Co–N(oxime) distances average 1.923(3), 1.898(3), and 1.900(3) Å for the order *cis*-Hao, *trans*-ao–H–ao, and *trans*-pnao showing only a slight, but significant, 0.02 Å lengthening in the *cis*-Hao case. The Co–N(amine) distances average 1.938(3), 1.946(3), and 1.977(3) Å respectively, with the *trans*-pnao complex longer, presumably due to steric strain caused by the ring containing the three carbon atoms. The C–C distances show the variations expected in going from sp^3 to sp^2 hybridization [in the range 1.505—1.537 Å (av.)]. The C–N(amine) distance is, as expected, slightly shorter than a C–C bond, having an average value of 1.502(4) Å, and no significant differences between the *cis* and *trans* complexes are seen. The multiple C–N bond distance is in the region found for other amineoxime cobalt(III) complexes [1.274(4), 1.280(4), and 1.276(3) Å respectively].

The N–O (oxime) distance changes significantly when the oxime oxygen is not hydrogen bonded, *i.e.* in the *cis* complex. In the *trans* complexes, which contain an intramolecular hydrogen bond, the N–O distance is 1.346(3) Å (av.) while in the *cis* analogue it is 1.396(3) Å. This is not accompanied by a distinct change in the adjacent C(3)–N(3) or C(4)–N(4) distances. The OH bond distance in the free oxime group (*cis* complex) is *ca.* 0.85 Å, considerably shorter than in the hydrogen-bonded complexes [1.22 Å (av.)] where the H atom is shared by two oxygens. The O(1)–O(2) distance in the *trans*-ao–H–ao complex is 2.423(3) Å, very close to that in the *trans*-pnao complex, 2.432(3) Å. The angles around the oxime nitrogens are close to 120°, ranging from 119.1 to 119.7° for the *trans* complexes and 117.8—118.8° for the *cis*. However the angles about the sp^2 carbons C(1) and C(2) deviate significantly in the range 115.3—124.0°.

The Co–N(nitro) distances are significantly different in the *trans* species [1.932(3) and 1.962(3)] while in the *cis* complex the sites are essentially identical with distances of 1.904(3) and 1.911(3) Å. The angles surrounding the cobalt atom are nearly octahedral with the N(amine)–Co–N(oxime) within a ligand being about 82.0° while the N(oxime)–Co–N(oxime) and N(amine)–Co–N(amine) angles between ligands are about 98.1 and 96.5° respectively. The nitro-N angles with respect to the metal atom are 90.6° and 179.6° for the *cis*-Hao and *trans*-ao–H–ao complexes respectively, very close to ideal. The O–N–O angles in the nitro groups are close to 120° in the three complexes (Tables 2 and 3) and the N–O distances vary slightly around the expected value of 1.22 Å. The dimensions of the nitrate ion in the *cis* complex are normal, with N–O distances ranging from 1.222 to 1.256 Å and angles in the range 118.9—121.8°.

trans-$[Co(ao–H–ao)Cl_2]$[14] is structurally similar to the *trans*-dinitro complex presented in this paper. The *trans*-chloride ions are at unequal distances from the metal [difference 0.008(1) Å], as is the case with the *trans*-dinitro complex, and the long bond is also related to the C(7)C(8) and C(9)C(10) methyl groups in the same manner.

Planes involving the Amineoxime Ligands.— The atoms Co,N(1),N(2),N(3),N(4) in *trans*-$[Co(ao–H–ao)(NO_2)_2]$ are in a well defined plane with deviations no greater than 0.02 Å. The plane Co,N(2),N(3),N(5),N(6) shows deviations no greater than 0.015 Å and the dihedral angle between these two planes is 89.09°. Deviations from the plane Co,N(1),N(2),N(3),N(4) are C(1) 0.046, C(2) 0.119, C(3) −0.072, C(4) −0.062, C(5) 0.196, C(6) 0.362, C(7) 1.038, C(8) 1.434, C(9) 1.046, C(10) 1.440, O(1) 0.062, O(2) 0.082, H(00) 0.122 Å. Thus the five-membered ring is slightly tilted with C(3) and C(4) closer to the N(5) side. The main conclusion is that the five-membered chelate ring is only slightly distorted from planarity, as for *trans*-$[Co(ao–H–ao)Cl_2]$ and much less than with the pnao analogue.

In the *cis* complex the N(1),N(3),N(4),N(6) atoms deviate from the least-squares plane including the cobalt atom by less than 0.05 Å. For both Hao ligands only their *gem* dimethyl groups deviate significantly from a planar arrangement (maximum deviation of any other atom, 0.10 Å). The dihedral angle between the nitro group planes has the value 82(1)°, similar to that found in the *trans*-dinitro ao–H–ao (89°) and *trans*-dinitro pnao complexes (90°).

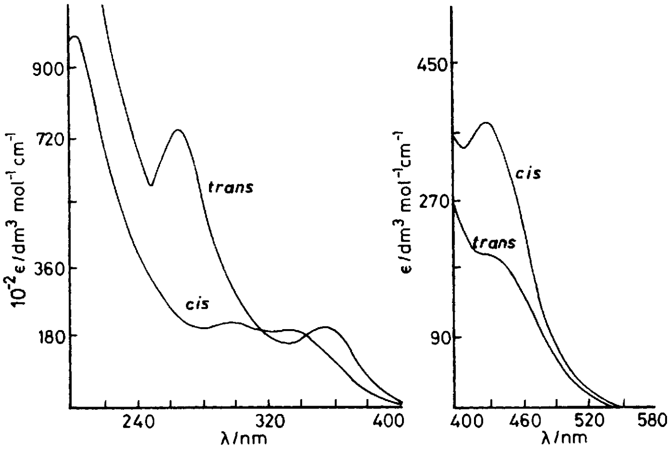

Figure 3. Visible and u.v. absorption spectra, in H_2O at 25 °C

Table 5. Rate of isotopic NO_2^- exchange with *cis*-$[Co(Hao)_2(NO_2)_2]^+$

$10^2[NO_2^-]$/ mol dm^{-3}	pH	T/°C	$t_{\frac{1}{2}}$/h	10^5k/s^{-1}
8.75	3.65	40	5.20	6.02
8.75	4.28	40	4.95	6.30
8.75	5.00	40	3.97	7.90
17.5	4.35	40	5.23	6.60
17.5	5.02	40	4.13	8.35
17.5	5.75	40	3.65	10.3
17.5	7.30	40	3.57	10.4
17.5	8.35	40	8.22	4.30
35.0	4.30	40	5.09	7.15
35.0	5.05	40	5.14	7.10
35.0	5.75	40	4.70	7.75
35.0	6.20	40	4.07	7.70
35.0	6.95	40	4.86	7.50
35.0	8.25	40	7.19	5.05
8.75[a]	4.30	40	4.94	6.30
8.75[a]	4.30	46.2	1.83	15.8
8.75[a]	4.30	25.1	37.7	0.830
8.75[a]	4.30	36.1	9.58	3.28
5—12.5[b]	5—9	40.0	~15	1.15—1.40

[a] I = 0.5 mol dm^{-3} ($NaNO_3$). [b] Data for *trans*-$[Co(ao\text{–}H\text{–}ao)(NO_2)_2]$; [complex] = 0.01 mol dm^{-3}.

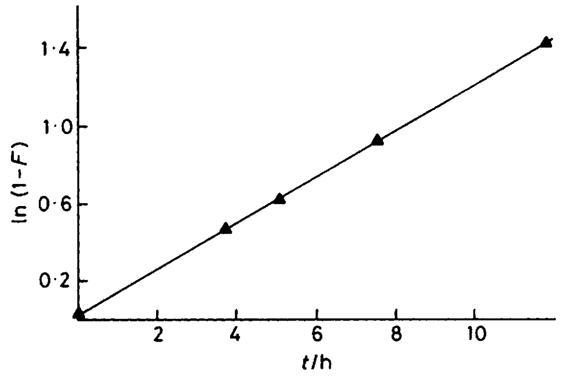

Figure 4. Representative McKay graph for $^{15}NO_2^-$ exchange with *cis*-$[Co(Hao)_2(NO_2)_2]$ in water. $[NO_2^-]$ = 0.175, [complex] = 3 × 10^{-3} mol dm^{-3}, pH = 4.4, T = 40 °C

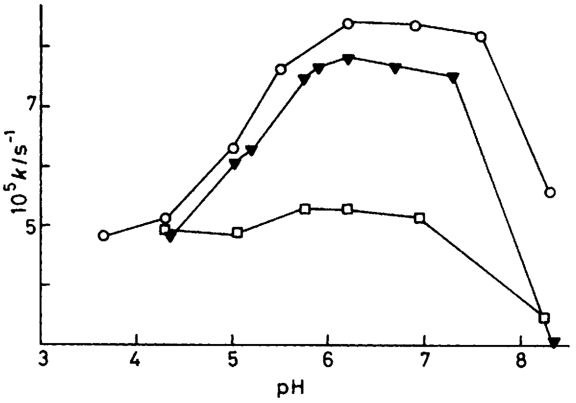

Figure 5. Plot of $k_{obs.}$ for NO_2^- exchange with *cis*-$[Co(Hao)_2(NO_2)_2]^+$ *versus* pH. $[NO_2^-]$ = 0.350 (□), 0.175 (▼), 0.087 mol dm^{-3} (○)

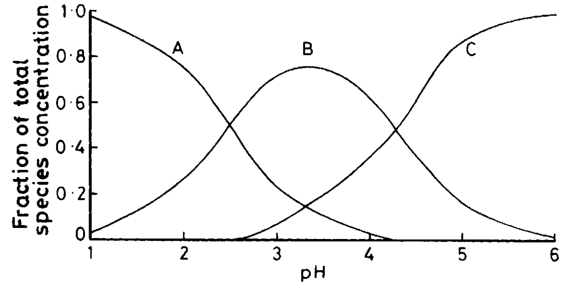

Figure 6. Species variation as a function of pH. pK_{a_1} = 2.6, pK_{a_2} = 4.4. A = *cis*-$[Co(Hao)_2(NO_2)_2]^+$, B = *cis*-$[Co(Hao)(ao)(NO_2)_2]$, C = *cis*-$[Co(ao)_2(NO_2)_2]^-$

Spectroscopic Properties.—The u.v.–visible spectra of the complexes are presented in Figure 3. They are remarkably similar in the visible region except for the smaller absorption coefficient for the *trans* molecule. At the natural pH of water solutions, both substances are predominantly in the zero-charged form. While larger differences exist in the u.v. region, they are not very useful since free NO_2^- and most other multi-atom ligands also absorb in this region.

The ^1H and ^{13}C n.m.r. spectra, summarized in Table 4, are primarily for identification. Clearly shown are the OHO protons at 19.1 p.p.m. downfield only for the *trans* complex, and the methyl groups. The NH proton signal is broad in the *trans* molecule indicating a rapid exchange process while extensive, sharp splitting occurs in the *cis* ion due in part to their non-equivalence and to nitrogen quadrupole splitting.

Rates of $^{15}NO_2^-$ *exchange.* Only *cis*-$[Co(Hao)_2(NO_2)_2]^+$ was investigated since complete studies of *trans*-$[Co(ao\text{–}H\text{–}ao)(NO_2)_2]$[11] and *trans*-$[Co(pnao)(NO_2)_2]$[8] were available for comparison. At constant temperature and pH the McKay graphs, ln (1 − F) *versus* time (t), Figure 4 (F = fraction reacted), were linear over at least three half-lives showing that, within experimental error, both nitro groups are kinetically equivalent. When the rate was followed with the ^{15}N enrichment in either the complex or in free NO_2^- it gave infinite values of ^{15}N corresponding to both NO_2^- groups exchanging.

The rate constant reported was generally reproducible to ±2% and was calculated from the slope ($k_{obs.}$) of the McKay graph by $k = (AB/A + B)k_{obs.}$, where A = 2[complex] and B = $[NO_2^-]$. The rate constant k was found to be sensitive to the solution pH, nature and concentration of the buffer and to $[NO_2^-]$. Table 5 gives some of these results. It is clear that, contrary to what was observed with the *trans*-ao–H–ao

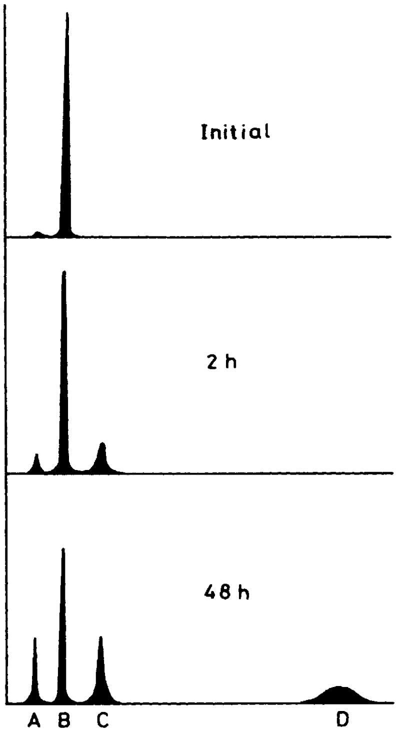

Figure 7. R.p.l.c. separation of reaction products of *cis*-$[Co(Hao)_2(NO_2)_2]^+$ with H_2O. pH 3.90, $T = 25$ °C, [complex] $= 4.5 \times 10^{-4}$ mol dm^{-3}. A = *trans*-dinitro, B = *cis*-dinitro, C = *cis*-aquanitro, D = *trans*-aquanitro

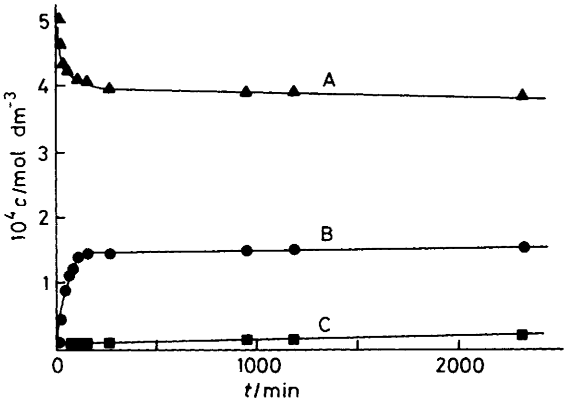

Figure 8. Species concentration changes with time, determined by r.p.l.c., A = *cis*-dinitro, B = *cis*-aquanitro, C = *trans*-dinitro. pH 5.9, $[\text{complex}]_{\text{initial}} = 5 \times 10^{-4}$, $[NO_2^-] = 4.38 \times 10^{-3}$ mol dm^{-3}

complex, this ion is highly susceptible to changes in its ionic environment. The pH dependency of the exchange rate constant is shown in Figure 5. There appears to be no direct correlation between the fractional amount of the three complex ion species present, Figure 6, and the pH dependency. During the kinetic measurements it was noted that the amount of precipitated complex decreased with the time of exchange, especially at low $[NO_2^-]$ or the extremes of pH, suggesting a chemical change. Since spectral methods in the visible region of the spectrum, Figure 7, are not sensitive, the different complexes were separated by r.p.l.c. and identified with known standards. Figure 8 contains some selected results showing the compositional changes with time. In addition to the *cis*- and *trans*-dinitro complexes, the *cis*- and *trans*-aquanitro complexes are formed. However, the presence of these new species does not directly affect the measured isotopic exchange rate constant because only the *cis*-dinitro complex is precipitated with BPh_4^- under the conditions used. Thus the measured exchange rate is that for *cis*-$[Co(Hao)_2(NO_2)_2]^+$ even though it is simultaneously changing to new species in major amounts.

Three significant observations can be made from the exchange data presented for *cis*-$[Co(Hao)_2(NO_2)_2]^+$. (*a*) The nitro groups show no observable kinetic differences. (*b*) The rate constant for exchange is larger than that for the analogous *trans*-ao–H–ao complex under comparable conditions. (*c*) The rate constant is sensitive to the solvent composition.

Estimates of the activation parameters at a pH of 4.3 and $[NO_2^-] = 8.75 \times 10^{-2}$ mol dm^{-3} from the temperature dependence of k gave values of $\Delta H^{\ddagger} = 107.4(60)$ kJ mol^{-1}, $\Delta S^{\ddagger} = +31.2(2)$ J K^{-1} mol^{-1}. These can be compared with those for the *trans*-dinitro complex of 122.9(21) kJ mol^{-1} and +54.3(4) J K^{-1} mol^{-1} respectively.

Discussion

The bond distances and angles involving the amineoxime ligands in the *cis*- and *trans*-dinitro complexes are very nearly the same. The two significant differences lie in the longer Co–N(oxime) distances in the *cis* complex and the N–O–H distances in the oxime groups. The former, apparently, is due to the *trans*-nitro groups which tend to weaken the bond opposite them. In the latter, the lack of the intramolecular hydrogen bond in the *cis* complex allows a shorter O–H bond and consequently a longer value for the N–O distance. The charge on the ion has little effect on the amineoxime ligand bonding.

The largest deviation between complexes is in the Co–NO_2 bonding. When the NO_2 groups are *trans* to each other the Co–N(NO_2) bonds are lengthened but not symmetrically. However as far as isotopic NO_2^- exchange kinetics show the nitro groups behave identically in contrast with the *trans*-dinitro-pnao complex.[8] It seems likely that asymmetry in the NO_2 positions produced by C(3) and C(4) being out of the CoN_4 plane is lost in the space of a few minutes in solution due to inversion around N(3) and N(4). This inversion would either be prevented or seriously inhibited by the three-carbon ring between N(3) and N(4) in the pnao complex.

The Co–N(NO_2) bond distances in *cis*-$[Co(Hao)_2(NO_2)_2]^+$ are about 1.91 Å, much shorter than in the *trans* complex or the *trans*-pnao complex but usual for either *cis*- or *trans*-ammine type complexes.[15]

If bond distance is related to bond strength and then to kinetic and thermodynamic stability, it would be expected that the *cis* complex is more stable to isotopic NO_2^- exchange than the *trans* isomer. The data in Table 5 show that this is not the case over a wide range of conditions. Also it is apparent that the *cis* isomer chemically changes in near-neutral solution to both the *cis*- and *trans*-aquanitro complexes and then ultimately to the *trans*-dinitro species. The aquation is much slower with the *trans* complex and is not favoured thermodynamically. On the basis of extended studies on the pH and $[NO_2^-]$ behaviour we have come to the conclusion that the *trans* isomer is kinetically more stable to both isotopic NO_2^- exchange and to chemical replacement of NO_2^- by water than is the *cis* isomer. The major pathway for the *cis* isomer reaction is *cis*-dinitro $\longrightarrow$ *cis*-aquanitro $\longrightarrow$ *trans*-aquanitro $\longrightarrow$ *trans*-dinitro. At the *cis*-aquanitro stage an isomerization also occurs producing at least one other geometric form of the *cis*-dinitro complex.

The rate constant for $^{15}N(NO_2^-)$ exchange is nearly uniform over the pH range 3.5—7.0 providing there is sufficient excess of NO_2^- to prevent extensive hydrolysis. Further, outside of this range, rapid irreversible dissociation of NO_2^-

occurs. At lower [NO_2^-] the rate constant increases especially in the less acidic region. This suggests that there is some reversible reaction of the *cis*-aquanitro species to give the *cis*-dinitro complex. If this series of equilibria were to be responsible for the enhanced exchange rate at high pH values and low [NO_2^-] then the *cis*-aquanitro ion would have to exchange its remaining [NO_2^-] at a relatively high rate compared to the base rate. This is indeed reasonable; it has been observed in other situations that enhanced substitution, racemization, and isomerization occur with hydroxo species presumably due to their ability to π-bond with the metal ion.

The partially reversible nature of the aquation of the *cis*-dinitro complex is also suggested by the r.p.l.c. studies in which a steady-state concentration of $[Co(Hao)_2(NO_2)(OH_2)]^{2+}$ is built up on a time-scale roughly comparable to that for NO_2^- exchange. At the pH values involved one would expect a significant fraction of the aquanitro complex to be in the hydroxonitro form thus facilitating the NO_2^- exchange of the aquanitro and thus the *cis*-dinitro species. The rate of NO_2^- exchange would thus be a composite rate of the intrinsic isotopic exchange rate and the reversible NO_2^- dissociation rate and one would not expect linear McKay plots. However, because of the difficulty in obtaining large numbers of points for the exchange curve, only about five points covering 1—2 half-lives were usually obtained and an appreciable non-linearity might not have been detected. Thus we suggest that the intrinsic exchange rate constant for the *cis*-dinitro complex is *ca.* 5×10^{-5} s^{-1} ($k_{obs.}$) at 40 °C and $I = 0.5$ mol dm^{-3} in the pH range 3.5—7.0 and that the presence of *cis*-aquanitro species generated by hydrolysis is responsible for the additional exchange at low NO_2^- and in the more basic region. Ultimately, the *cis*-aquanitro ion rearranges to the *trans* form irreversibly which then quickly converts to the final thermodynamically stable *trans*-dinitro complex. Thus, the question is why is the *cis*-dinitro complex so much more sensitive to NO_2^- hydrolysis than the *trans* isomer. It is tempting to relate the kinetic stability of the *trans* complex to the intramolecular hydrogen bond and the singular non-ionic species which prevails.

The *trans* isomer, which has a zero charge, is almost devoid of these effects. There is little evidence either chemically or isotopically to support any mechanism for NO_2^- replacement on a cobalt(III) centre and these results, while they limit the possibilities, do not provide any definitive mechanistic conclusions. However, it does appear clear that bond distances of the leaving group are not closely related to kinetic lability and it suggests that mechanistic paths are of primary concern.

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