Control of Axial–Equatorial Interactions in (Dimethylglyoximato)cobalt(III) Complexes. Part 1. Counter Cation Effect on the Strength of the Intramolecular Hydrogen Bond, OH · · · O$^-$, of *trans*-Bis(dimethylglyoximato)dinitrocobaltate(III) Anions and Crystal Structure of the Tetramethylammonium Salt†

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The infrared frequencies observed for the particular functional group of both the axial and the equatorial ligands of the complex anion $[Co(Hdmg)_2(NO_2)_2]^-$ (H_2dmg = dimethylglyoxime) have been found to be widely different upon changing the counter cations M^+ (M = Li, Na, K, Rb or Cs) or NR_4^+ (R = H, Me, Et or Bu). In particular, the O–H stretching frequency of the intramolecular hydrogen bond, O–H · · · O$^-$, changes markedly depending on the kind of counter cation. Alkali-metal counter cations, M^+, would exert a co-ordination effect upon the donor atom in the complex anion, while tetraalkylammonium counter cations would give a predominantly long-range potential effect only. In order to investigate the difference in the counter cation effects on the strength of the in-plane intramolecular hydrogen bond, crystal and the molecular structures of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ and $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$ were compared. An unusual conformation around the Co–NO_2^- moiety was observed in $[NMe_4][Co(Hdmg)_2(NO_2)_2]$. The orientation of the axial ligands, NO_2^-, is restricted in such a way that they are located over the five-membered chelate ring formed by the $Hdmg^-$ moiety and the Co^{III} atom. On the other hand, $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$ has a usual conformation which would lead to minimum non-bonded interaction between the $Hdmg^-$ moiety and the two axial ligands, NO_2^-. In this conformation, two NO_2^- are positioned over the pseudo-six-membered chelate rings. A further important structural feature in $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ is a very long Co–NO_2^- distance [1.974(3), as compared with 1.949(3) and 1.943(3) Å in the sodium salt]. This difference is ascribed to the counter cation effect. The stretching frequencies of O–H · · · O$^-$ and C=N in $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ are quite different from those in $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$. These facts suggest that the counter cations play an important role in controlling the axial–equatorial interactions in $[Co(Hdmg)_2(NO_2)_2]^-$.

Recently, interest in the axial–equatorial interactions in bis(dimethylglyoximato)cobalt(III) complex ions, $[Co(Hdmg)_2(base)_2]^n$, has been considerably increased from the viewpoint of the structural and dynamic features.[1] The electronic structure of the central cobalt(III) atom in $[Co(Hdmg)_2(base)_2]^n$ strongly depends on the type of axial base. The electronic effects of the axial base are transmitted to the equatorial $Hdmg^-$ moiety through the Co^{III}. Thus, the static and the dynamic properties of the equatorial ligands are primarily influenced by the electronic properties of the axial ligand. In general, the strength of the intramolecular hydrogen bond in $[Co(Hdmg)_2(base)_2]^n$ in solution is controlled by the basicity, the charge and the π-back-bonding ability of the axial base; the axial base primarily has the ability to control the axial–equatorial interactions in the complex ion. However, this type of interaction does not always occur in the solid. Although the stretching frequency of the O–H · · · O$^-$ hydrogen bond depends strongly on the nature of the axial base,[1] the ν(O–H · · · O$^-$) observed for $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ was found to be quite different from that for $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$.[2] A preliminary report has demonstrated that the molecular structure of these two complexes are quite different.[3] Furthermore, IR study of a series of $M[Co(Hdmg)_2(NO_2)_2]$ and $[NR_4][Co(Hdmg)_2(NO_2)_2]$ complexes with various counter cations (M = Li, Na, K, Rb or Cs; R = H, Me, Et or Bu) clearly demonstrates that the axial–equatorial interations in the solid state are largely affected also by the nature of the counter ions. The size, hydrophobicity and/or the co-ordination ability of the counter cation would play an important role in the control of the axial–equatorial interactions in $[Co(Hdmg)_2(NO_2)_2]^-$.

In the present article we report the characteristic difference in the crystal and the molecular structure between $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ and $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$ together with IR studies of various $M[Co(Hdmg)_2(NO_2)_2]$ and $[NR_4][Co(Hdmg)_2(NO_2)_2]$ complexes.

Experimental

Reagents.—Dimethylglyoxime was purchased from Wako Pure Chemical Ind., Ltd., sodium hexanitrocobaltate(III) and alkali-metal chlorides (LiCl, RbCl and CsCl) from Nakarai Chemicals, Ltd. Tetraalkylammonium chlorides (NMe_4Cl, NEt_4Cl and NBu_4Cl) (Tokyo Kasei) were used without further purification.

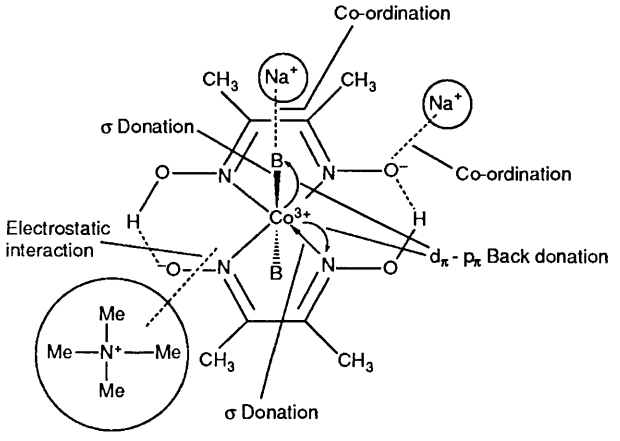
Preparation of the Complexes.—The salt $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$ was prepared from $Na_3[Co(NO_2)_6]$ and dimethylglyoxime.[4] To an aqueous solution of $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$ was gradually added a saturated aqueous solution of an alkali-metal chloride (MCl). Yellowish brown

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Cation effect on the infrared spectra (cm^{-1}) of $M[Co(Hdmg)_2(NO_2)_2]$–nH_2O and $[NR_4][Co(Hdmg)_2(NO_2)_2]\cdot nH_2O$

M^+ or NR_4^+	n	ν(O–H ··· O)	ν(C=N) [δ(H_2O)][a]	ν(N–O)		ν(NO_2^-) asym	ν(NO_2^-) sym
NH_4^+	1	1758	1554 [1634w]	1238	1088	1410	1316
NMe_4^+	0	1768	1568	1242	1096	1402	1316
NEt_4^+	0	1770	1578	1240	1098	1404	1314
NBu_4^+	1	1780	1576	1242	1094	1412	1312
Li^+	4		1568 [1634s]	1238	1092	1420	1322
Na^+	2	1744	1558[b] [1630s]	1236	1090	1426	1322
		1746[c]	1556[b] [1630m]	1236	1090	*d*	1322
K^+	2	1732	1566 [1636]	1240	1092	1420	1322
Cs^+	0.5	1734	1568	1240	1088	1418	1322
Rb^+	0.5	1734	1566	1240	1088	1416	1318

[a] s = Strong, m = medium and w = weak. [b] The peak splits into doublet. [c] In Nujol mull. [d] Overlapped by Nujol band.



Scheme 1 B = Base

crystals or powder were precipitated within a few minutes. The tetraalkylammonium salt of the complex was prepared by adding a concentrated solution of NR_4Cl to an aqueous solution of $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$. Dark brown columnar crystals appeared within a few hours. The elemental analyses of the crystals thus formed coincide with the formulae $Li[Co(Hdmg)_2(NO_2)_2]\cdot 4H_2O$, $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$, $K[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$, $Rb[Co(Hdmg)_2(NO_2)_2]\cdot 0.5H_2O$, $Cs[Co(Hdmg)_2(NO_2)_2]\cdot 0.5H_2O$, $[NH_4][Co(Hdmg)_2(NO_2)_2]\cdot H_2O$, $[NMe_4][Co(Hdmg)_2(NO_2)_2]$, $[NEt_4][Co(Hdmg)_2(NO_2)_2]$ and $[NBu_4][Co(Hdmg)_2(NO_2)_2]\cdot H_2O$.

Measurements.—A stock solution of $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$ and $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ was freshly prepared by dissolving the corresponding salt in doubly distilled water. It does not keep for more than 12 h. Equilibrium and kinetic measurements were described in the previous paper.[1]

Crystallography.—Crystals of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ were obtained by adding a concentrated solution of NMe_4Cl to a dilute aqueous solution of $Na[Co(Hdmg)_2(NO_2)_2]\cdot 2H_2O$.

Crystal data. $C_{12}H_{26}CoN_9O_8$, M 455.31, monoclinic, space group $C2/c$, a = 11.334(3), b = 12.263(4), c = 14.987(4) Å, β = 102.38(4)°, U = 2034.6 Å^3, Z = 4, D_c = 1.486 g cm^{-3}.

A single crystal with dimensions of about 0.2 × 0.4 × 0.5 mm was used. The cell dimensions and reflection intensities were measured on a four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), using the ω–2θ scanning mode. Three standard reflections measured at intervals of every 100 reflections showed no significant decrease in intensity during the course of data collection. The intensities were corrected for Lorentz and polarization factors, but not for absorption or extinction. Up to 2θ ≤ 55°, 1910 independent structure factors above the 3σ(F) level were selected for the structure determination. The structure was solved by the heavy-atom method, and refined by the block-diagonal least-squares method with anisotropic thermal parameters. After all hydrogen atoms had been located in a Fourier difference map, full-matrix least-squares refinements were carried out including the hydrogen atoms. The final R and R' values were 0.048 and 0.056 for 1910 reflections. The maximum and minimum residuals in the final Fourier difference map were 0.5 and −0.6 e Å^{-3}, respectively.

The X-ray measurements were performed on a Rigaku diffractometer at the High-Brilliance X-Ray Laboratory of Hokkaido University, and the calculations were done on a HITAC M-280H computer at the Computing Center of Hokkaido University.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond intensity and angles.

Results and Discussion

IR Measurements of the Various $M[Co(Hdmg)_2(NO_2)_2]$ *and* $[NR_4][Co(Hdmg)_2(NO_2)_2]$ *Complexes.*—The observed infrared frequencies of the particular functional group in both the axial (NO_2^-) and the equatorial ligands ($Hdmg^-$) in the series of $M[Co(Hdmg)_2(NO_2)_2]$ and the $[NR_4][Co(Hdmg)_2(NO_2)_2]$ complexes differ widely upon changing the counter cations, M^+ and NR_4^+ (Table 1). All the IR spectra of the complexes exhibit a weak broad band around 1750 cm^{-1}. This band has been shown to be due to the O–H stretching frequency of the intramolecular hydrogen-bridged O–H ··· O$^-$ bond.[5] It is strongly dependent upon the electronic properties of the axial ligand.[1] However, in the system investigated here, ν(O–H ··· O$^-$) varies considerably from 1732 to 1780 cm^{-1} depending on the counter cation. In particular, the value for $Na[Co(Hdmg)_2(NO_2)_2]$ is smaller than that of $[NR_4][Co(Hdmg)_2(NO_2)_2]$, indicating the presence of a stronger intramolecular hydrogen bond in the former complex.

The band around 1560 cm^{-1} could be attributed to the C=N stretching frequency of the equatorial $Hdmg^-$.[6] Burger and Ruff[7] pointed out that a lower-frequency shift of ν(C=N) is correlated with stronger d_π(Co)–p_π(C=N) bonding, resulting in an increase in conjugation of the five-membered chelate rings formed by the co-ordinated $Hdmg^-$ and Co^{III}.[1] This back donation enhances the increase in electron density of the C=N and N–O bond as shown in Scheme 1. Therefore, the strong axial–equatorial interactions would result in shifts to higher frequency of the N–O vibration and shifts to lower frequency of the C=N and O–H ··· O$^-$ vibrations. This expected correlation is clearly observed in the NR_4^+ counter cation systems (Fig. 1). The value of ν(O–H ··· O$^-$) increases linearly with increase of

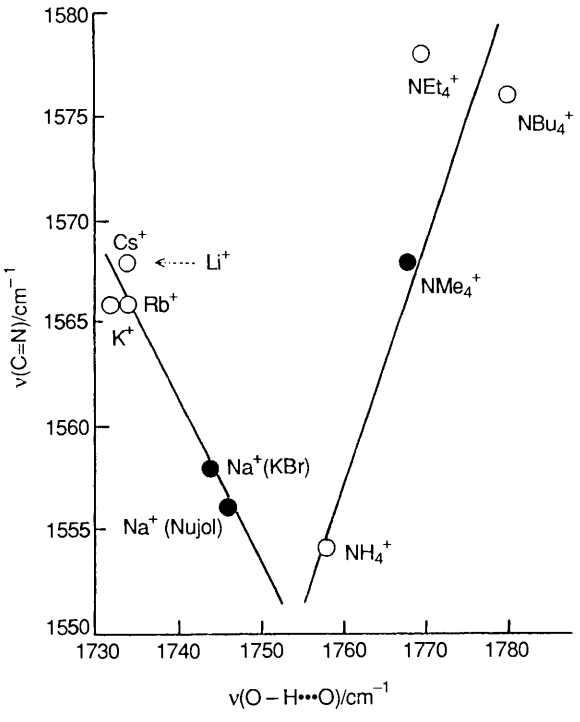


Fig. 1 Plot of ν(C=N) *vs.* ν(O–H • • • O) for the various bis(dimethylglyoximato)cobalt(III) complexes $M[Co(Hdmg)_2(NO_2)_2]\cdot nH_2O$ and $[NR_4][Co(Hdmg)_2(NO_2)_2]\cdot nH_2O$. The ν(O–H • • • O) band of the lithium salt is too broad to determine the exact value. The closed circles denote the stretching frequencies, ν(C=N) and ν(O–H • • • O), of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ and $Na[Co(Hdmg)_2(NO_2)_2]$

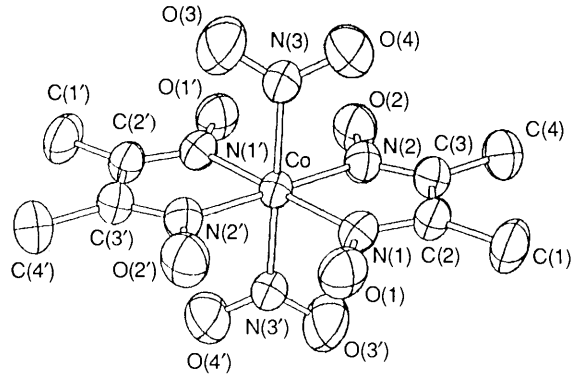


Fig. 2 Perspective view of the complex anion of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$, showing the molecular structure and the atomic labelling scheme. Hydrogen atoms have been omitted for clarity

ν(C=N). In general, the stronger the intramolecular hydrogen bond the lower is the value of ν(O–H • • • O⁻). The intramolecular hydrogen bond is weakened with decrease in conjugation of the five-membered chelate rings. This tendency almost corresponds to that of the increase in the size of the NR_4^+ cation. The increase in the distance $NR_4^+ \cdots [Co(Hdmg)_2(NO_2)_2]^-$ would be closely correlated with the modulation of the axial–equatorial interactions which lead to weakening of the intramolecular hydrogen bond and/or reduced conjugation in the five-membered chelate rings. In the M^+ system, all the points except one (M = Na) are clustered together. This may simply be a result of the structural change $(Hdmg)_2 \longrightarrow H_2dmg{\cdot}dmg$. X-Ray crystallographic studies show that Na^+ co-ordinates with the oxygen atom of the N–O of the $Hdmg^-$ and the NO_2^- (see below). This $Na^+ \cdots O$ co-ordination both in the equatorial and in the axial positions would reduce the electron density in the N–O bond, leading to a weaker intramolecular hydrogen bond. Thus, the value of ν(O–H • • • O⁻) of the sodium salt should be much larger than that of the other salts (Li^+, K^+, Rb^+ or Cs^+). It is noteworthy that two different types of correlations between ν(C=N) and ν(O–H • • • O⁻) are observed in the $[NR_4][Co(Hdmg)_2(NO_2)_2]$ and $M[Co(Hdmg)_2(NO_2)_2]$ systems.

The NO_2^- ions of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ and of $Na[Co(Hdmg)_2(NO_2)_2]$ co-ordinate to Co^{III} in the nitro form (X-ray crystallographic study). The free NO_2^- ion exhibits an asymmetric stretching (ν_{asym}) and a symmetric frequency (ν_{sym}) at 1250 and 1335 cm^{-1}, respectively.[8d] The complexes of the type $[M(NO_2)_6]^{n-}$ (M = Co^{II}, Ni^{II}, Ir^{III} or Rh^{III}) exhibit ν_{asym} and ν_{sym} bands in the regions 1343–1425 and 1306–1340 cm^{-1}, respectively.[9] The values of ν_{asym} and ν_{sym} of $[Co(NO_2)(NH_3)_5]^{2+}$ have been determined to be 1428 and 1310 cm^{-1}.[10] Therefore, the ν_{asym} band tends to shift markedly to higher frequency upon co-ordination, whereas ν_{sym} shifts a little. From these considerations, the strong bands at 1402–1426 and 1312–1322 cm^{-1} observed for $M[Co(Hdmg)_2(NO_2)_2]$ and in $[NR_4][Co(Hdmg)_2(NO_2)_2]$ complexes can be assigned to ν_{asym} and ν_{sym}, respectively (Table 1). These bands are not observed for other $Co(Hdmg)_2(base)_2$ complexes (base ≠ NO_2^-). The ν_{asym} band is shifted significantly whereas ν_{sym} changes little upon changing the counter cation. The values of ν_{asym} in the alkali–metal cation systems are larger than those in the tetraalkylammonium systems, suggesting a stronger co-ordination of NO_2^- to Co^{III} in the former case.

Finally, the IR spectra of $Na[Co(Hdmg)_2(NO_2)_2]$ and $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ are compared with each other as the representatives of the alkali-metal and the tetramethylammonium cation systems. The values of both ν(OH • • • O⁻) and ν(C=N) (1744 and 1558 cm^{-1}) of the former complex are appreciably smaller than those (1768 and 1568 cm^{-1}) of the latter complex, suggesting for the sodium salt a stronger intramolecular hydrogen bond and extensive conjugation of the five-membered chelates formed by the $Hdmg^-$ and Co^{III} in the $[Co(Hdmg)_2(NO_2)_2]^-$ anion. The role of Na^+ and NMe_4^+ in the axial–equatorial interaction of the $[Co(Hdmg)_2(NO_2)_2]^-$ anion would be very different from each other. The tetramethylammonium ion is of interest because of its bulkiness (r_s = 2.05 Å and r = 3.4 Å)* and symmetrical shape with low surface charge density, while the sodium ion (r_s = 1.83 Å) could interact only with the particular oxygen atoms of the complex anion [in aqueous solution Na^+ is bonded to about four water molecules at 2.4 Å (ref. 12)]. Therefore, the outer-sphere cation effects on the axial–equatorial interactions in $[Co(Hdmg)_2(NO_2)_2]^-$ would be quite different in the NMe_4^+ and the Na^+ systems. Furthermore, the value of ν_{asym} of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ is smaller than that of $Na[Co(Hdmg)_2(NO_2)_2]$, showing that the co-ordination of NO_2^- to Co^{III} is much weaker. This weaker co-ordination of NO_2^- is also indicated by the X-ray crystallographic studies (see below). Thus, the co-ordination strength of the axial ligand NO_2^- to the central Ci^{III} of other complexes can be predicted from the value of $\nu_{asym}(NO_2^-)$.† The nitro-N ligand is unperturbed in the tetraalkylammonium salts owing to the relatively hydrophobic 'greasy' nature of these counter cations. In this instance a relatively weak bonding configuration is observed between cobalt and nitro-N. For alkali-metal counter cations, however, which bridge between the axial and equatorial ligands, a stronger Co–N(NO_2) interaction is observed.

Structural Comparison between $[NMe_4][Co(Hdmg)_2(CO_2)_2]$ *and* $Na[Co(Hdmg)_2(NO_2)_2]$.—The molecular structure of the complex anion of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ is shown in Fig. 2, and selected bond lengths and angles are given in Fig. 3. The final atomic positional parameters are presented in Table 2.

* The symbols r and r_s denote the radius estimated from the molecular volumes and from the limiting molarity by Stokes law, respectively.[11]

† Details on the correlation between the structure and the stretching frequency of NO_2^- in other cobalt(III) complexes (M = Li, K, Rb or Cs; NR_4^+ = NEt_4^+, NPr_4^+ or NBu_4^+) will be reported elsewhere.

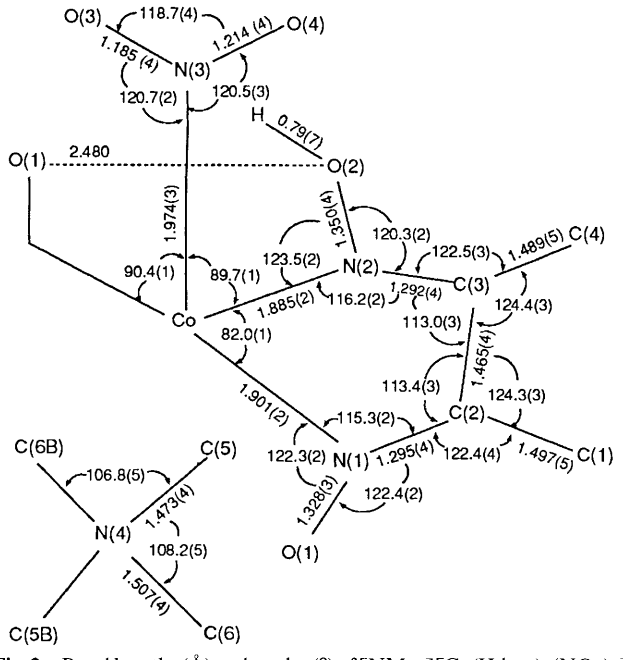


Fig. 3 Bond lengths (Å) and angles (°) of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$

Table 2 Final atomic parameters ($\times 10^4$) of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$

Atom	*x*	*y*	*z*
Co	2500	2500	0
O(1)	1394(2)	440(2)	118(2)
O(2)	4993(2)	3078(2)	576(2)
O(3)	1503(4)	3573(4)	1291(3)
O(4)	2737(4)	2412(3)	1893(2)
N(1)	2420(2)	1000(2)	304(2)
N(2)	4152(2)	2287(2)	518(2)
N(3)	2223(2)	2899(2)	1215(2)
N(4)	5000	5744(4)	2500
C(1)	3522(5)	−587(3)	1047(3)
C(2)	3431(3)	571(2)	725(2)
C(3)	4451(3)	1332(3)	857(2)
C(4)	5706(4)	1058(5)	1340(3)
C(5)	4430(7)	6405(6)	1704(4)
C(6)	5990(9)	5073(8)	2240(6)

The cobalt atom lying on a centre of symmetry is coplanar with the N_4 atoms in the equatorial position (Fig. 3). The two $Hdmg^-$ moieties are approximately planar and linked by two intramolecular OH · · · O^- hydrogen bonds. In Table 3 the lengths of the corresponding bonds of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ and $Na[Co(Hdmg)_2(NO_2)_2]$[13] are compared. The bond length in $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ (2.480 Å) is appreciably shorter [Δr(OH · · · O^-) = 0.037 Å] than that of $Na[Co(Hdmg)_2(NO_2)_2]$ (av. 2.517 Å). The N–O, Co–N(NO_2^-) and O–H bond lengths are quite different from each other. These results are in accord with the IR data mentioned above. The increase in electron density on the O^- would lead to a lengthening of the O–H and the O · · · O^- bonds. However, the other bond lengths [Co–N(C=N), C=N, C–Me] are almost the same. The frequency ν(C=N) in the IR spectra is very sensitive to a change in the axial–equatorial interaction depending on the counter cation, but the C=N bond length is not sensitive.

The Co–N(NO_2^-) bond of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ [1.974(3) Å] is appreciably longer than that of $Na[Co(Hdmg)_2(NO_2)_2]$ [av. 1.946(9), 1.943(3) and 1.949(3) Å]. In the analogous complex, *trans*-dinitro[2,2′-trimethylenediiminobis-(2-methylbutan-3-one oximato)]cobaltate(III),[14a] in which the equatorial ligand differs from $(Hdmg)_2$ by having one $CH_2CH_2CH_2$ instead of an OH · · · O^- bridge, the two NO_2^- group planes are nearly perpendicular, owing to the steric interactions of the propylene bridge with one NO_2^- group. Furthermore the Co–NO_2 bond lengths are not equal [1.937(3) and 1.984(3) Å]. The shorter value has been assumed as the 'normal' one on the basis of the Co–NO_2 distances in other cobalt complexes. The normal Co–NO_2 bond length was reported to be 1.935(11) Å for $[Co(NO_2)_2(NH_3)_4]NO_3·H_2O$.[14b] An unusually longer Co–NO_2 distance was also reported for $[Co(Hdmg)_2(NO_2)(PPh_3)]$ as 1.980(9) Å.[13] In the latter case the lengthening of the Co–NO_2 bond could be attributed to the *trans* effect of the PPh_3 group. Interestingly, the cobalt atom is displaced by 0.042 Å toward the P atom from the plane formed by the equatorial N_4 atoms. In our case, the longer Co–NO_2 bond in $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ is suggested by the smaller ν_{asym} value. This lengthening is caused by the outer-sphere counter cation effects which lead to the change in the axial–equatorial interaction.

Another structural difference is observed with respect to the co-ordination mode of the equatorial ligand. As for the intramolecular hydrogen bond observed in the $[Co(Hdmg)_2(base)_2]^-$ anion, three types of formulations are considered as shown in Scheme 2. The NMe_4^+ salt is found to be formulated usually as $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ containing two monoanionic $Hdmg^-$ (type **A**). Such a formulation has been reported for various other $Co(Hdmg)_2$ complexes,[15] as well as $[Fe(Hdmg)_2(Him)_2]·2MeOH$ (Him = imidazole),[16] $[Ni(Hdmg)_2]$[17] and $[Cu(Hdmg)_2]$.[18] On the other hand, the sodium salt can be formulated as $Na[Co(H_2dmg)(dmg)(NO_2)_2]·2H_2O$[13] (type **B**). The differences between $[Co(Hdmg)_2]^-$ and $[Co(H_2dmg)(dmg)]^-$ are relatively subtle, depending on the location of the bridging H atoms.[19] Formulation **B** has also been observed in other systems such as $[Co(H_2dmg)(dmg)Cl(H_2NC_6H_4Cl\text{-}4)]·2H_2O$ and $[Co(H_2dmg)(dmg)Cl(H_2NC_6H_4SO_2NH_2\text{-}4)]·H_2O$[20] arising from the π interaction between the benzene ring and the dmg^{2-} moiety. Interestingly, the H_2dmg moiety deviates appreciably from planarity. Further, the Co–N(dmg^{2-}) bond length and that of Co–N(H_2dmg) range from 1.870(5–8) to 1.884(5–8) and from 1.896(8) to 1.908(5) Å, respectively. In our system, there is no π interaction between the $Hdmg^-$ moiety and the axial NO_2^- group. Therefore, the unusual equatorial co-ordination mode (type **B**) as found in the sodium system would be caused by the counter cation effects. Thus, the change in the counter cation effects leads to a change in the axial–equatorial interaction of the $[Co(Hdmg)_2(NO_2)_2]^-$ moiety. Perhaps, the double-minimum potential curve for the intramolecular hydrogen bond, O–H · · · O^-, would be affected considerably by a change in the axial–equatorial interaction through the central cobalt(III) atom. Thus, a change in the counter cation would cause a change in the formulation as $[Co(Hdmg)_2]^n$ and/or $[Co(H_2dmg)(dmg)]^n$.

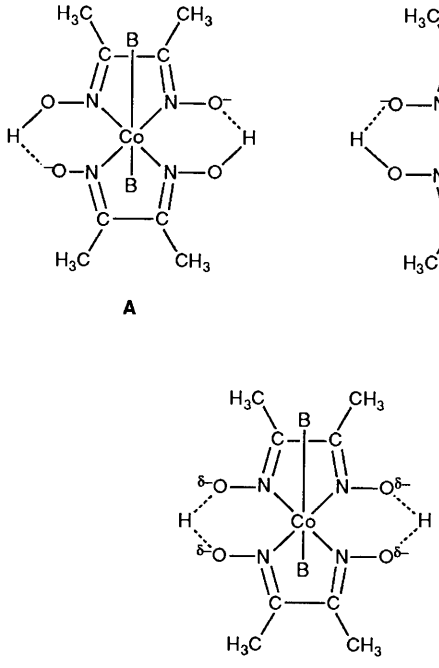
Orientation of the Axial Base, NO_2^-.—The two axial bases, NO_2^-, in $Na[Co(Hdmg)_2(NO_2)_2]$ are disposed nearly on the line separating the two oximes (Fig. 4). The dihedral angle φ between the planes passing through the Co, N(3), O(3), O(4) and N(3′), O(3′), O(4′) atoms is 12.3°.[13] On the other hand, the planes of the nitro groups in $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ dissect each $Hdmg^-$ moiety in the conformation * shown in Fig. 4. The dihedral angle between the mean planes passing through Co, N(3), O(3), O(4) and Co, N(3′), O(3′), O(4′) is *ca.* 0°. This unusual orientation of the axial bases leads to an appreciably longer Co–N(NO_2) bond. It should be noted that the unusual orientation of the axial base could be attributed only to the difference in the counter cation effect between NMe_4^+ and Na^+.

* The most unusual structural feature of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ is the orientation of the two axial NO_2^- bases which are disposed over the five-membered chelate rings of the $Hdmg^-$ moiety. On the other hand, the two NO_2^- in $Na[Co(Hdmg)_2(NO_2)_2]$ lie over pseudo-six-membered chelate rings with the OH · · · O bonds (usual conformation).

Table 3 Comparison of bond lengths (Å) for $[NR_4][Co(Hdmg)_2(NO_2)_2]$ and $Na[Co(H_2dmg)(dmg)(NO_2)_2]\cdot 2H_2O$

Complex		Co–N(NO_2)	Co–N(Hdmg)	N–O	N=C	=C–CH_3	=C–C=	O–H
$[NMe_4][Co(Hdmg)_2(NO_2)_2]$		1.974(3)	1.885(2)	1.350(4)	1.292(4)	1.489(5)	1.465(4)	0.79(7)
			1.901(2)	1.328(3)	1.295(4)	1.497(5)		
$Na[Co(H_2dmg)(dmg)(NO_2)_2]\cdot 2H_2O$[a]	b	1.949	1.918(2)	1.371(4)	1.295	1.496	1.494	0.98
			1.918(2)	1.366(3)	1.297	1.496		0.82
	c	1.943	1.902(2)	1.353(3)	1.301	1.497	1.482	
			1.903(2)	1.350(4)	1.297	1.507		

[a] Ref. 13. [b] Bond length for H_2dmg. [c] Bond length for dmg^{2-}. [d] Values in parentheses represent the estimated standard deviations (e.s.d.s). The e.s.d.s for N=C, =C–CH_3, =C–C= and O–H were not specified in ref. 13.



Scheme 2

The N–O(NO_2^-) bond lengths [1.230–1.250(4–5) Å] in the sodium counter cation system are larger than those [1.185(4) and 1.214(4) Å] in the NMe_4^+ system. A similar situation was observed in the control of the spin state of (porphyrinato)iron(III) complexes[21] and also for the unusual bond lengths and the conformation of some B_{12} models.[22] Bis(3-chloropyridine)-(2,3,7,8,12,13,17,18-octaethylporphyrinato)iron(III) perchlorate $[Fe(oep)(3Cl\text{-}py)_2]ClO_4$ was isolated in two crystalline forms, monoclinic and triclinic.[21b] The Fe–N(3Cl-py) bond length in the former complex [2.310(17) Å] is much larger than that in the latter [av. 2.194(2) Å]. This lengthening is attributed to the orientation of the axial base (3Cl-py) with respect to the equatorial porphyrinato core. Furthermore, the dihedral angle of two 3Cl-py in the triclinic and monoclinic forms is 41 and 5.7–13.9°, respectively. This situation is very similar to our case. Such an unusual bond length and conformation have been observed also in some vitamin B_{12} model compounds.[22b] The Co–N(py) bond length of $[Co(salphen)(py)(CH_2CN)]\cdot H_2O$ [salphen = *o*-phenylenebis(salicylideneiminate)] is 2.098(4) Å and py lies over the six-membered chelate ring (the normal conformation). However, the py of $[Co(salphen)(py)Et]\cdot H_2O$ is disposed over the five-membered chelate ring made by the phenylenediamine moiety. Marzilli and co-workers[22b] explained these phenomena in terms of the very long Co–N(py) bond in the latter complex [2.215(4) Å].

Control of the Axial–Equatorial Interaction by Counter Cation.—The difference in the orientation and the bond length

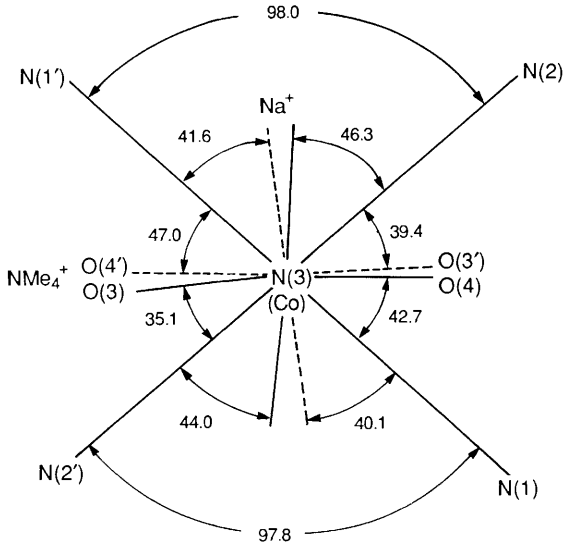


Fig. 4 Orientation of the axial bases, NO_2^-, relative to the $Hdmg^-$ moiety with bond angles (°), in $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ and $Na[Co(H_2dmg)(dmg)(NO_2)_2]$

as mentioned above is attributed to the difference in the interaction mode between the complex anion $[Co(Hdmg)_2(NO_2)_2]^-$ and the counter cations Na^+ and NMe_4^+. The sodium ion could interact with the O(4) and O(3′) atoms of NO_2^- [$r(Na^+ \cdots O)$ = 2.433(3) and 2.445(3) Å], the apical O(1) atom of the $Hdmg^-$ (2.433 Å), and the oxygen atoms of two water molecules [2.358(4) and 2.292(10) Å]. The five-co-ordination around the Na^+ is distorted square-planar pyramidal. The above $Na^+ \cdots O$ distances are in the range of those reported for similar ionic compounds in the solid state[22] and are comparable with those for $[Na(OH_2)_4]^+$ ion in solution. The $r(Na^+ \cdots O)$ for $[Na(OH_2)_4]^+$ has been estimated to be 2.40(3)[12] and 2.42 Å[23] by X-ray diffraction study. Thus, the co-ordination of the oxime oxygen to the counter cation is now established judging from the value of $r(Na^+ \cdots O)$. Perhaps, Na^+ could exert an electronic effect on the $[Co(Hdmg)_2(NO_2)_2]^-$ moiety through co-ordination of the oxime oxygen and the NO_2^- oxygen. On the other hand, NMe_4^+ could not interact with a particular oxygen atom in the $[Co(Hdmg)_2(NO_2)_2]^-$ moiety and could exert only an electrostatic long-range effect as shown in Fig. 5. Thus, the counter cations Na^+ and NMe_4^+ differ in their ability to control the axial–equatorial interactions in the $[Co(Hdmg)_2(NO_2)_2]^-$ anion. An extended X-ray absorption fine structure study is now in progress in order to clarify the counter cation effects on the electronic structure of the $[Co(Hdmg)_2(NO_2)_2]^-$ anion. Recently, related phenomena have been observed in some cobalt(III) complexes. Comparisons of X-ray absorption near-edge spectra have been made for $[Co(NH_3)_6]X_3$ (X = Cl, Br or I). The shapes of the Co K edge spectra are considerably dependent on the counter anion.[24] Furthermore, the d–d transition band and the chemical shift of the carboxyl carbon

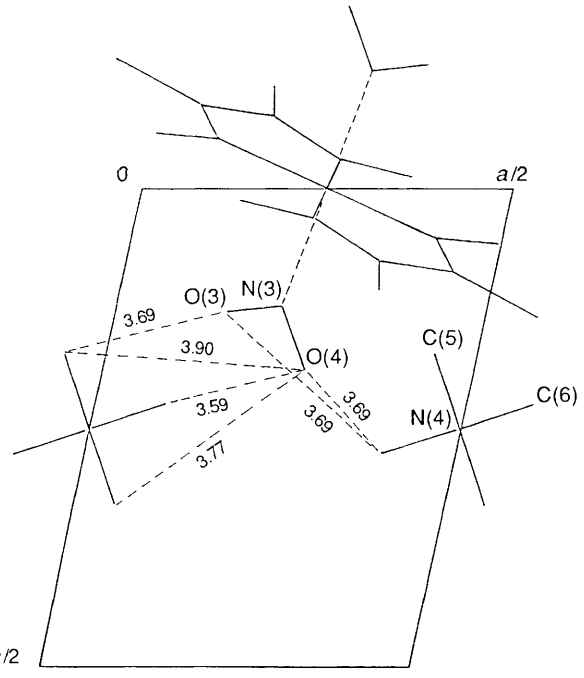


Fig. 5 View of the structure of $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ along the *b* axis. Interatomic distances (Å) between the NMe_4^+ cation and the $[Co(Hdmg)_2(NO_2)_2]^-$ anion are depicted

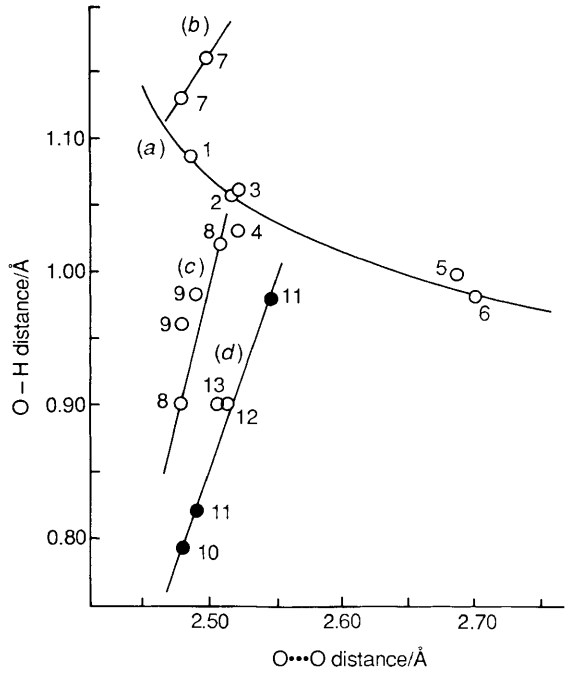


Fig. 6 Correlation between the O–H and O···O distances. 1, KH_2PO_4; 2, $(CO_2H)_2{\cdot}2H_2O$; 3, KH_2AsO_4; 4, KD_2AsO_4; 5, α-HIO_4; 6, $CaSO_4{\cdot}H_2O$; 7, $[Co(H_2dmg)(dmg)Cl(H_2NC_6H_4Cl\text{-}4)]{\cdot}2H_2O$;[20] 8, $[Co(H_2dmg)(dmg)(H_2NC_6H_4SO_2NH_2\text{-}4)]{\cdot}H_2O$; 9. $[CoH_2dmg)(dmg)(NH_3)Cl]$;[22a] 10, $[NMe_4][Co(Hdmg)_2(NO_2)_2]$; 11, $Na[Co(H_2dmg)(dmg)(NO_2)_2]{\cdot}2H_2O$; 12, $[Co(Hdmg)_2L]$ [L = (*S*)-1-cyanoethyl-(*S*)(−)-α-methylbenzylamine];[15] 13, $[Co(Hdmg)_2(PBu_3)L]{\cdot}H_2O{\cdot}MeOH$ (L = 2,6-dihydroxypurine).[15] The closed circles denote the values for $[NMe_4][Co(Hdmg)_2(NO_2)_2]$ and $Na[Co(Hdmg)_2(NO_2)_2]$

atom of $K[Co(edta)]{\cdot}2H_2O$ (edta = ethylenediaminetetraacetate) are strongly dependent on the acceptor number of solvents such as Me_2SO, MeCN, $CHCl_3$, EtOH, MeOH and water. These data clearly demonstrate that the environment at the periphery of the complex ion plays an important role in determining the electronic properties of that ion.[25]

Relationship between the OH···O$^-$ and O–H *Bond Distances.*—The $[Co(Hdmg)_2(NO_2)_2]^-$ complex anion has two symmetrical (type **A** in Scheme 2; 10, 12 and 13 in Fig. 6) or two asymmetrical intramolecular O–H···O$^-$ hydrogen bonds (type **B** in Scheme 2; 7–9 and 11 in Fig. 6). Some relationships between the structural and the electronic factors which affect the strength of the intramolecular O–H···O$^-$ hydrogen bond are expected. For linear hydrogen bonds such as O–H···O, O–H···N, N–H···F, N–H···O, N–H···Cl, N–H···N and F–H···F a linear relationship holds between X–H···Y distance and the X–H stretching frequency. However, for bent systems a large deviation from the regular sequence was observed.[8] In general, the covalent X–H bond length in an asymmetric hydrogen bond is influenced by the strength of the H···Y contact: a shorter H···Y contact will generally lead to a longer X–H distance.[8c] For the strong intermolecular hydrogen bonds of some compounds the X–H distance has been found to increase inversely as the X–H···Y distance decreases, which are shown in curve (*a*) of Fig. 6.[8a] In the case of the intramolecular hydrogen-bond system of $[Co(Hdmg)_2(NO_2)_2]^-$ there is a fascinating direct correlation in that the O–H distance increases linearly with increasing O···O distance. This correlation results in the three lines (*b*)–(*d*) of Fig. 6. At the present stage of our X-ray investigation, the structural differences which might explain explicitly the different dependences, direct *vs.* inverse, between the bond distances in groups (*a*) and (*b*)–(*d*) are thought to be the differences in the type of hydrogen bond, intra *vs.* inter-molecular.

Since the length of the rigid Co–N(oxime) bond is not much affected by the change in the axial base and the counter cation, the O···O distance varies only a little [r(O···O) = 2.47–2.55, Δr(O···O) = 0.08 Å]. On the other hand, the O–H bond length varies appreciably [r(O–H) = 0.79–1.16, Δr(O–H) = 0.37 Å]. The electron density on the O$^-$ in the O–H···O$^-$ hydrogen bond is greatly affected by a change in the axial base [1] and the counter cation. The increased electron density due to the axial–equatorial interaction leads to a stronger O–H···O$^-$ intramolecular hydrogen bond. Therefore, as the O–H···O$^-$ bond becomes stronger, the O–H bond length is expected to increase more drastically than the O···O distance. Such a correlation is clearly observed as the sharp dependence of r(O–H) on r(O···O) [curves (*b*)–(*d*) of Fig. 6].

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