Very Short OHO Hydrogen Bonds in a Binuclear Transition-metal Complex. Neutron-diffraction Study at 120 K of $[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3\cdot0.5H_2O$‡

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A structural determination of $[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3\cdot0.5H_2O$ has been carried out at 120 K by neutron diffraction: a = 12.059(9), b = 8.700(7), c = 16.477(14) Å, β = 121.86(3)°, space group $P2/c$, and Z = 2. Binuclear cations made up of tris chelates are linked by very short hydrogen bonds: $R(O\cdots O)$ = 2.390(7), r(O–H) = 1.195(4); $R(O\cdots O)$ = 2.429(6), r(O–H) = 1.204(7), 1.228(7) Å. The results show that a previous *X*-ray diffraction study provided an inadequate description of the structure, since it was unable to resolve disorder of the water molecule (which had been misplaced), of one of the perchlorate groups, and of one of the neutral ligands; the superiority of low-temperature neutron diffraction in the resolution of disorder at this level is demonstrated. The i.r. spectrum is discussed in relation to the nature of the proton potential well.

Few examples of strong hydrogen bonds formed by chelating ligands in transition-metal complexes are known. A division may be made between intramolecular and intermolecular hydrogen bonds. In the former case, the best known example concerns the quadridentate ligand $HON{=}CMeCMe_2NH(CH_2)_2NHCMe_2CMe{=}NOH$, which is able to wrap around metal ions such as Ni^{II}, Co^{II}, Cu^{II}, *etc.* and form O–H–O bonds upon loss of a proton.[1] The formation of complexed metal dimers through intermolecular hydrogen bonds was first suggested by Yoneda and Kida,[2] and the subject has been expanded in recent years by Bertrand and Eller.[3]

Single-crystal *X*-ray diffraction has shown the existence of co-operative hydrogen bonding in, for example, 2-aminoethanol complexes of Cu^{II},[4] Co^{III},[5] and Ni^{II} [5] [$R(O\cdots O)$ = 2.434, 2.542; 2.38, 2.445; and 2.73, 2.68 Å]. Schiff-base ligands prepared from aminoalcohols form similar polynuclear complexes.[6]

Apart from the inherent interest of the role of the hydrogen bridge and the nature of the potential energy curve for the proton, magnetic interactions between paramagnetic ions are possible. Significant antiferromagnetic coupling has been reported, notably in $[Cu\{HO(CH_2)_2NC(Me)CH_2C(Me)N(CH_2)_2O\}_2]$,[6] which is thought to proceed *via* the bridging hydrogen. Pathways for superexchange involving the proton are less well defined than those for the well known involvement of the hydrogen bond in the phase transitions of certain classes of ferroelectrics. Some hydrogen bonds are surprisingly short, in particular the oxygen–oxygen distance (2.30 Å) in the last-mentioned copper complex is physically questionable and it is likely that there are unaccounted for disorder problems.

The compound $[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3\cdot0.5H_2O$ was selected from other members of this family for neutron-diffraction study in an attempt to correlate the i.r. absorption band and the geometry of the hydrogen bond. This work has produced detailed information concerning unusual disorder of one of the aminoethanol groups, which was not detected by *X*-ray diffraction. The *X*-ray study also failed to reveal the disorder around one of the perchlorate ions and the water molecule, which had been misplaced.

Experimental

Syntheses.—$[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3\cdot0.5H_2O$. The salt $Co(ClO_4)_2\cdot6H_2O$ (3.66 g, 0.010 mol) was dissolved in methanol (99.99%, 50 cm^3), to which a solution of 2-aminoethanol (1.83 g, 0.030 mol) in methanol (99.99%, 25 cm^3) was added. (*NB*: the preparation in ref. 5 describes the addition of concentrated phosphoric acid at this stage. We found this to be unnecessary.) After several days at room temperature, slow evaporation of the solvent afforded small, well formed, dark purple crystals which could be recrystallised from water. Repeated filtering of the mother-liquor, retention and reimmersion of the largest and best-formed crystals produced approximately hexagonal plates suitable for neutron diffraction (Found: C, 18.45; H, 5.00; N, 10.6. Calc. for $[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3\cdot0.5H_2O$: C, 18.25; H, 5.00; N, 10.65%).

$[Co\{H_2N(CH_2)_2O\}_3]\cdot3H_2O$. The complex was prepared by stirring for 24 h a solution of $CoCl_2$ (6 g, 0.046 mol) and 2-aminoethanol (30 cm^3, 0.050 mol) in 85% aqueous ethanol. The violet precipitate was washed with 85% aqueous ethanol (Found: C, 24.55; H, 8.00; N, 14.15. Calc. for $[Co\{H_2N(CH_2)_2O\}_3]\cdot3H_2O$: C, 24.55; H, 8.20; N, 14.35%).

Infrared Spectra.—Crystalline material was finely ground, mulled with Nujol, and mounted between KBr windows. Spectra were recorded using a Nicolet MX-1 FT spectrometer operated at room temperature in a humidity-controlled environment. The background was subtracted. The spectral resolution was 1 cm^{-1} over the entire range (4 800—400 cm^{-1}).

Neutron Diffraction.—A plate-like crystal of the compound was mounted along its *b* axis on the D9 diffractometer at the

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‡ Tris(2-aminoethanol-*NO*)tris(2-aminoethanolato-*NO*)dicobalt(III) triperchlorate–water (2/1).

Supplementary data available (No. SUP 56436, 6 pp.): thermal parameters, least-squares plane, i.r. spectra. 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. Crystal data and experimental details of the structure determination for $[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3\cdot0.5H_2O$

M	788.8
Space group	$P2/c$
Unit-cell constants at 120 K	
a/Å	12.059(9)
b/Å	8.700(7)
c/Å	16.477(14)
β/°	121.86(3)
D_c/g cm^{-3}	1 468.2
Z	2
Crystal dimensions	1.86 × 1.92 × 1.60 mm for plate centre to plate edge, depth 1.2 mm
U/mm^3	16.26
λ/Å	0.84
Angular range/°	$2 < 2\theta < 70$
μ/cm^{-1}	1.40
Scan mode	ω—2θ
Detector aperture/mm	14
Sample–detector/cm	40

Institut Laue Langevin. Once centred in a Displex cryostat and the orientation matrix determined at ambient temperature, the temperature was slowly lowered to 120 K. The crystal mosaicity was checked at 120 K (ω scan) and the unit cell constants at this temperature were refined. Using a neutron-beam wavelength of 0.84 Å, intensity data were collected to $\theta_{max.} = 35°$, with standard reflections monitored every 40 reflections. Throughout the experiment, the temperature was maintained at 120 ± 0.02 K. Crystal data and experimental details are given in Table 1.

Data reduction and structure refinement. Data reduction was carried out with the minimum $\sigma(I)/I$ method[7] and the data were corrected for absorption effects and the Lorentz factor. Of 3 831 reflections collected, 3 216 were unique and used in the initial refinements. The scattering lengths were taken from ref. 8. Refinements, using SHELX 76,[9] were started using all the non-hydrogen-atom positions as determined by X-ray diffraction.[5] The unweighted R factor after three cycles was 0.40, which was reduced to 0.24 after introduction and refinement of the hydrogen-atom co-ordinates from ref. 5. At this stage, all thermal factors were isotropic, but several additional features (regions of highly positive and highly negative nuclear density) could be seen on Fourier difference syntheses, and it was obvious that the X-ray result[5] was an incomplete description of the crystal structure.

First, in one of the perchlorate groups, the atom Cl(2) appears to lie on the two-fold axis. In ref. 5 two oxygen-atom positions were reported, such that, by symmetry across the axis, the perchlorate group appears completely ordered. In the present work, two additional peaks of nuclear density could be refined as oxygens, so that the perchlorate group is disordered by axial symmetry. Initial site occupancy factors of 0.5 assigned to all atoms were subsequently refined to 0.50(1) and the R factor showed significant improvement to 0.18. Nevertheless, the situation was still not wholly satisfactory since the O(54)–Cl(2) distance was unrealistically long. A physically meaningful distance was obtained by relaxing the axial positional constraints for Cl(2).

Secondly, in the X-ray study, the water molecule was determined only by the position of the oxygen, the hydrogens remaining undetected. The appearance of strongly negative peaks corresponding to these hydrogens in Fourier difference maps from neutron diffraction assisted in locating the water molecule: whereas in ref. 5 the oxygen was reported to lie on the two-fold axis, our neutron data indicate that, instead, one hydrogen atom lies on this axis, and that the oxygen and other hydrogen are disordered on either side of it, with a site occupancy of 0.25(1). Resolution of this additional disorder problem associated with the axis reduced the R factor to 0.10, all atoms having refined anisotropic thermal parameters.

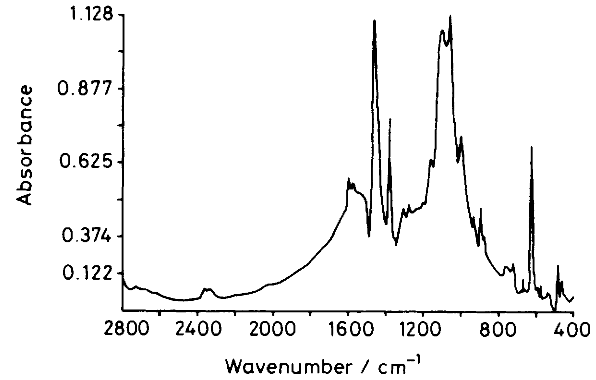

Figure 1. Infrared spectrum of $[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3\cdot0.5H_2O$

Thirdly, examination of Fourier difference maps showed a distinct second site for one of the carbons [C(31)] in one of the chelate rings. Ligand disorder was not found in ref. 5, although a disorder model was used for $[Ni_2\{H_2N(CH_2)_2OH\}_2\{H_2N(CH_2)_2O\}_4][ClO_4]_2$.[5] Neutron diffraction has provided additional support for the disorder in the present case, as the positions of several supplementary hydrogen atoms around carbon and nitrogen allow the nature of the disorder to be elucidated (Figure 3). An ideal geometry for this 'additional' ring 3 was calculated from the average bond lengths and angles of the two ordered rings 1 and 2, and the atomic co-ordinates refined using geometrical constraints (SHELX DFIX option). After convergence, it was subsequently considered as a rigid group and refined using the well-separated carbon atom, C(31), as pivot. Refinement of the site-occupancy factors for the two disordered sites converged to 0.77(1) and 0.23(1) (referred to hereafter as chelates '3A' and '3C' respectively) and anisotropic thermal parameters were allowed only for the atoms in ring 3A.

Employing full-matrix least-squares refinement, and only those reflections for which $F > 3\sigma(F)$, a formal extinction parameter was refined. Finally, 18 weak reflections with $I < 3\sigma(I)$ were suppressed, and a Fourier difference map calculated at this stage showed some residual density in the region of the perchlorate group not affected by the disorder, of the order ± 0.1 of that for an oxygen atom on the same scale. The final residuals were $R = \Sigma\Delta F/\Sigma F_o = 0.066$, $R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.057$, with the weighting scheme $w = k[\sigma^2(F_o) + 0.0004\,F_o^2]^{-1}$.

Results and Discussion

Infrared Spectra.—The i.r. spectrum of $[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3\cdot0.5H_2O$ is shown in Figure 1. The spectra of the non-hydrogen-bonded neutral cobalt(III) compound $[Co\{H_2N(CH_2)_2O\}_3]\cdot3H_2O$ and of $[Ni_2\{H_2N(CH_2)_2OH\}_2\{H_2N(CH_2)_2O\}_4][ClO_4]_2$ are available as SUP 56436. For $[Co\{H_2N(CH_2)_2O\}_3]\cdot3H_2O$, no crystal data are available, but an octahedron around cobalt of three nitrogen and three oxygen atoms has been assumed from u.v.–visible spectra.[2] The ν(N–H) modes are superimposed on the broad ν(O–H) band arising from symmetric and antisymmetric stretching modes of the water molecule. Any intermolecular hydrogen-bonding interaction between water molecules is obviously weak. Skeletal modes for the ligand are sharply defined.

Table 2. Positional parameters (× 10^4). In this and all other Tables, the standard deviations in parentheses refer to the least significant figure

Atom	x	y	z	Atom	x	y	z
Co	−2 053(5)	2 644(7)	2 216(4)	HO(1)[e]	0(0)	4 400(7)	2 500(0)
C(11)	−1 359(3)	4 496(3)	3 783(2)	HO(2)	−471(5)	1 730(6)	1 585(4)
C(12)	−1 030(3)	5 429(3)	3 161(2)	HN(1A)	−2 535(6)	2 640(7)	3 539(4)
C(21)	−3 605(3)	3 106(3)	241(2)	HN(1B)	−3 303(6)	4 080(7)	2 817(4)
C(22)	−2 240(3)	2 768(3)	473(2)	HN(2A)	−3 180(5)	4 866(7)	1 197(4)
C(31)[a]	−2 368(3)	−268(4)	2 811(3)	HN(2B)	−4 342(5)	3 746(7)	1 087(4)
C(32)[a]	−935(3)	−126(4)	3 142(3)	HN(3AA)	−3 995(7)	950(7)	1 857(6)
C(33)[b]	−2 157(7)	−486(7)	2 407(5)	HN(3BA)	−3 206(8)	303(9)	1 360(5)
C(34)[b]	−1 059(7)	105(7)	3 364(5)	HN(3AC)	−3 783(7)	690(7)	1 250(5)
N(1)	−2 454(2)	3 461(2)	3 134(1)	HN(3BC)	−3 584(7)	896(7)	2 323(5)
N(2)	−3 465(2)	3 743(2)	1 130(1)	H(11A)	−1 614(6)	5 229(8)	4 203(4)
N(3A)[a]	−3 085(5)	791(7)	1 959(4)	H(11B)	−524(6)	3 770(8)	4 272(4)
N(3C)[b]	−3 105(7)	798(7)	1 957(5)	H(12A)	−81(6)	6 018(7)	3 593(5)
O(1)	−989(3)	4 412(3)	2 503(2)	H(12B)	−1 784(6)	6 310(6)	2 764(5)
O(2)	−1 595(3)	1 917(3)	1 340(2)	H(21A)	−4 187(5)	2 034(7)	52(4)
O(3A)[a]	−636(5)	1 486(7)	3 244(4)	H(21B)	−4 112(6)	3 913(7)	−353(4)
O(3C)[b]	−685(7)	1 576(7)	3 216(5)	H(22A)	−1 713(6)	3 848(7)	559(5)
OW[c]	−4 582(12)	658(14)	2 904(11)	H(22B)	−2 269(6)	2 087(8)	−103(4)
O(41)	−2 031(4)	1 643(6)	4 903(3)	H(31A)	−2 708(8)	−1 439(8)	2 614(9)
O(42)	−3 793(4)	786(4)	5 003(3)	H(31B)	−2 534(7)	104(10)	3 367(6)
O(43)	−3 853(8)	3 082(11)	4 311(9)	H(32A)	−307(8)	−702(10)	3 842(8)
O(44)	−2 546(13)	2 730(12)	5 915(9)	H(32B)	−757(7)	−660(8)	2 612(7)
O(51)[d]	−4 610(6)	2 100(7)	−1 946(4)	H(33A)	−2 623(7)	−1 530(7)	2 430(5)
O(52)[d]	−4 286(5)	3 684(7)	−2 969(4)	H(33B)	−1 671(7)	−667(7)	1 994(5)
O(53)[d]	−4 965(6)	4 753(7)	−2 955(4)	H(34A)	−197(7)	−612(7)	3 655(5)
O(54)[d]	−3 591(5)	3 163(8)	−1 663(4)	H(34B)	−1 402(7)	221(7)	3 872(5)
Cl(1)	−3 067(5)	2 059(2)	5 020(2)	HW(1)[c]	−4 016(28)	444(32)	−6 642(20)
Cl(2)[d,*]	−5 085(3)	3 420(3)	−2 580(4)	HW(2)	−5 000(0)	−336(20)	−7 500(0)

Occupancy factors: [a] 0.77(1); [b] 0.23(1); [c] 0.25(1); [d] 0.49(1); [e] set at 0.5. * See text.

For $[Co_2\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3][ClO_4]_3 \cdot 0.5H_2O$, as described below, there are two crystallographically independent hydrogen bonds. Although one is constrained by space-group symmetry to be centred, even for the other the difference between the two O–H distances is close to the 3σ limit of the standard deviations. The hydrogen atom can be considered therefore as being not far from the centre of the O • • • O bond. The i.r. band profile is reminiscent of a type (ii) spectrum in Hadži's classification,[10] often observed for solid acid salts of carboxylic acids having symmetrical or nearly symmetrical hydrogen bonds, for which there is a virtual continuum below 1 600 cm^{-1} (D band). From Figure 1 it is seen that the strong absorption due to N–H and O–H stretching found for the pure alcohol [ν_{asym}(N–H) 3 352, ν_{sym}(N–H) 3 287 cm^{-1} superimposed on the broad ν(O–H) centred at 3 050 cm^{-1}] has been shifted to lower wavenumbers, and the most striking feature is the band extending from *ca.* 1 700 to 800 cm^{-1}.

Specific assignment of all the features in this band is unnecessary, and it will only be mentioned that sharp CH_2 vibrations and those arising from the C–N and C–O in the ligand framework appear at frequencies close to those of the unchelated alcohol. Of interest however are the possible assignments for the stretching [ν(OH)] and in- and out-of-plane bends [δ(OH) and γ(OH)] of the hydrogen bond. It is possible to distinguish two sub-maxima at *ca.* 1 550 and *ca.* 1 240 cm^{-1}, but given that the hydrogen-bond lengths are within 0.04 Å of each other, it seems unjustified to assign the maxima to one or other bond, or to the components resulting from their i.r. ν(O–H) coupling.

For strong hydrogen bonds, the 'Evans effect' (ref. 11) is well documented and several examples in many different types of system are known.[12] This arises from the interaction of a broad level ν(O–H) with a narrow skeletal mode, and produces sharp transmission windows in the spectrum. In the present case we note a sharp minimum at 1 490 cm^{-1} and it is possible that ν(O–H) lies in this range. Such an assignment would be consistent with a short, but asymmetrical hydrogen bond. For example, the i.r. absorption maximum of $KH(CH_3CO_2)_2$ occurs at 1 350 cm^{-1},[13] and the O • • • O bond has a non-centred H atom, $R = 2.476$ Å.[14] The ν(O–H) mode for very short, symmetrical bonds is generally found at lower frequencies, < 800 cm^{-1}. The submaxima at 1 550 and 1 240 cm^{-1} could then be assigned to δ(OH) and γ(OH) respectively.

In the case of $[Ni_2\{H_2N(CH_2)_2OH\}_2\{H_2N(CH_2)_2O\}_4][ClO_4]_2$, prepared according to the published procedure,[5] type (ii) absorption is absent and instead a broad band at 3 000—1 600 cm^{-1} is found. Having three discernible maxima, the spectrum corresponds to the ABC-type spectrum well known for strong and medium strong hydrogen bonds.[10] The maximum of the ν(O–H) absorption occurs in the range 2 680—2 720 cm^{-1}; absorption at this higher frequency is consistent with the considerably longer hydrogen bonds in the crystal, 2.68(5) and 2.73(2) Å.[5]

Neutron Diffraction.—Table 2 lists the positional parameters for all the atoms. As expected, there is a considerably improved precision compared with the *X*-ray results, particularly for those atoms for which the *X*-ray study had been unable to resolve structural disorder. A perspective view of the cation is shown in Figure 2, together with the numbering scheme used in the Tables. The nomenclature used in ref. 5 has been retained. As described in ref. 5, each of the aminoethanol ligands chelates cobalt through the amino nitrogen and the hydroxyl group, and the co-ordination around each cobalt is a distorted octahedron. Bond distances and angles within the cobalt co-ordination sphere are given in Table 3: these are identical, within the estimated standard deviations (e.s.d.s) to those in ref. 5.

Strong hydrogen bonds link two $Co\{H_2N(CH_2)_2O\}_3$

Table 3. Bond lengths (Å) and angles(°) around cobalt

	$n = 1$	$n = 2$	$n = 3$ ring A	$n = 3$ ring C
Co–N(n)	1.949(8)	1.948(5)	1.942(6)	1.948(9)
Co–O(n)	1.896(7)	1.907(9)	1.936(7)	1.852(8)
O(n)–Co–N(n)	85.6(3)	86.0(3)	85.8(3)	87.3(4)

O(1)–Co–O(2)	91.6(4)	O(2)–Co–N(3C)	88.6(4)
O(1)–Co–N(2)	88.8(3)	O(3A)–Co–N(1)	88.7(3)
O(1)–Co–O(3A)	92.0(3)	O(3C)–Co–N(1)	87.8(4)
O(1)–Co–O(3C)	91.0(3)	O(3A)–Co–N(2)	176.7(5)
O(1)–Co–N(3A)	177.8(3)	O(3C)–Co–N(2)	177.6(6)
O(1)–Co–N(3C)	178.3(3)	N(1)–Co–N(2)	94.6(3)
O(2)–Co–N(1)	177.2(4)	N(1)–Co–N(3A)	94.5(3)
O(2)–Co–O(3A)	90.8(4)	N(1)–Co–N(3C)	94.1(4)
O(2)–Co–O(3C)	91.7(4)	N(2)–Co–N(3A)	93.4(2)
O(2)–Co–N(3A)	88.2(3)	N(2)–Co–N(3C)	92.9(3)

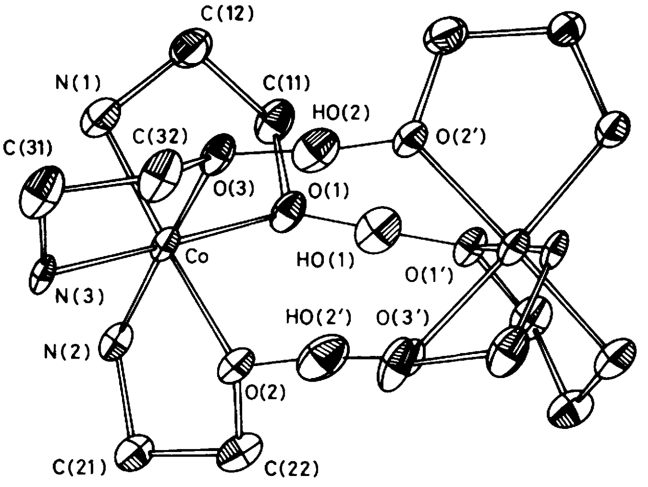

Figure 2. ORTEP diagram of the dimeric cobalt cation. Thermal ellipsoids at 50% probability. For clarity, only one of the disordered chelates (3A) is shown, and only the hydrogen-bonding hydrogens

moieties. The neutron-diffraction results have confirmed the short O ··· O interactions determined by the X-ray study, with an improved precision. The geometries of the two crystallographically independent hydrogen bonds, obtained in this work and in ref. 5, are compared in Table 4. The shortest hydrogen bond is that constrained by space-group symmetry to be centred. A Fourier difference map calculated with this hydrogen removed gave no indication of disorder, and the proton is thus considered as occupying a single potential minimum.

Few hydrogen bonds O–H ··· O having R(O ··· O) less than 2.40 Å have been reported. For other polynuclear complexes bridged by hydrogen bonds, a shorter O ··· O distance has been reported only for copper(II) or nickel(II) complexes chelated by a Schiff-base ligand formed by the condensation of 2-aminoethanol and 2,4-pentanedione which, despite its large e.s.d., is one of the shortest intermolecular OHO bonds known.[6]

It is of interest to consider the different results concerning the proton potential energy curve. Our neutron results clearly give little or no indication of a strongly asymmetric location for the hydrogen. On the other hand, the i.r. maximum does not occur at a low enough frequency, by comparison with a large number of other systems, for this system to be classified as having a symmetrical potential energy curve. We conclude that, in this case, spectroscopy permits a more sensitive analysis and that the proton energy well tends to statistical symmetry over crystal space.

Table 4. Geometry of the hydrogen bonds (distances in Å, angles in°)

	X-Ray[a]	Neutron
O(1) ··· O(1′)[b]	2.396(10)	2.390(7)
O(1)–HO(1)	1.198(7)	1.195(4)
O(1)–HO(1)–O(1′)	169(6)	179.0(3)
O(2) ··· O(3)	2.447(7)	2.429(6)
O(2)–HO(2)	0.99(8)	1.204(7)
O(3)–HO(2)	1.46(8)	1.228(7)
O(2)–HO(2)–O(3)	172(7)	174.3(6)

[a] Values other than O ··· O distances were calculated using the coordinates from ref. 5. [b] O(1′) is related to O(1) through $-x, y, \frac{1}{2} - z$.

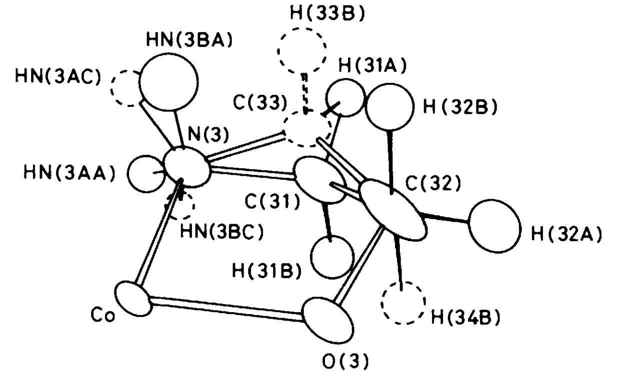

Figure 3. The disordered chelate ring 3. Dotted circles represent atoms with site occupancy 0.23

A view of the disordered chelate ring 3 is shown in Figure 3. Here, for the sake of clarity, only carbon atom C(33) and the hydrogen atoms H(33B) and H(34B), HN(3AC) and HN(3BC), which have positions clearly distinct from their 3A partners, have been represented. The others are shown as a single site which produces bridging hydrogens H(31A) and H(32A). The distance between the two disordered carbons, C(31)–C(33), is 0.849(11) Å. The nature of the disorder is somewhat analogous to that described[5] for $[Ni_2\{H_2N(CH_2)_2OH\}_2\{H_2N(CH_2)_2O\}_4][ClO_4]_2$, where residual electron density in the vicinity of the chelates revealed by Fourier difference maps led to the introduction of supplementary positions for oxygen, nitrogen, and one of the carbons. Similarly, an X-ray determination of the mixed-metal complex $[CoNi\{H_2N(CH_2)_2OH\}_3\{H_2N(CH_2)_2O\}_3]I_2$[15] indicated disorder for oxygen and nitrogen.

Bond distances and angles for all of the rings are collected in Table 5. This includes the (refined) bond lengths to hydrogens, which had been placed in calculated positions in ref. 5. The standard deviations of these values are approximately half those determined by X-ray diffraction. For each of the five-membered rings (including the Co atom) only the carbon atom nearest the nitrogen is out of the plane, all other atoms lying within 0.08 Å of the plane. Such an arrangement is in contrast to that observed for bichelating ethylenediamine ligands, where a zigzag arrangement of atoms alternately above and below the least-squares planes is the rule. Likewise, using published atomic co-ordinates for $[\{Cu[H_2N(CH_2)_2OH]_2[H_2N(CH_2)_2O]_2\}_2]$-

Table 5. Bond lengths (Å) and angles (°) in the ions

(*a*) Cation

			$n = 3$	
	$n = 1$	$n = 2$	ring 3A	ring 3C
N(*n*)–C(*n*1)	1.485(3)	1.490(4)	1.512(4)	1.487(4)
C(*n*1)–C(*n*2)	1.515(5)	1.510(4)	1.517(6)	1.516(8)
C(*n*2)–O(*n*)	1.421(5)	1.422(4)	1.436(7)	1.420(10)
HN(*n*A)–N(*n*)	1.017(7)	1.022(6)	1.028(9)	1.015(8)
HN(*n*B)–N(*n*)	1.023(6)	1.021(7)	1.013(9)	1.036(14)
H(*n*1A)–C(*n*1)	1.098(9)	1.108(7)	1.082(8)	1.079(10)
H(*n*1B)–C(*n*1)	1.098(6)	1.093(6)	1.086(12)	1.120(14)
H(*n*2A)–C(*n*2)	1.104(6)	1.101(7)	1.110(10)	1.083(10)
H(*n*2B)–C(*n*2)	1.102(6)	1.103(8)	1.105(13)	1.118(14)
Co–N(*n*)–C(*n*1)	106.8(3)	108.1(3)	108.5(2)	105.7(5)
N(*n*)–C(*n*1)–C(*n*2)	106.8(2)	106.4(2)	105.6(3)	106.4(5)
C(*n*1)–C(*n*2)–O(*n*)	108.0(2)	107.5(3)	106.9(4)	108.1(6)
C(*n*2)–O(*n*)–Co	113.8(4)	111.4(3)	110.8(3)	113.0(5)
HN(*n*A)–N(*n*)–HN(*n*B)	106.8(6)	106.4(6)	107.7(7)	108.5(9)
HN(*n*A)–N(*n*)–C(*n*1)	108.1(3)	108.6(5)	105.8(5)	116.4(7)
HN(*n*B)–N(*n*)–C(*n*1)	108.6(4)	110.8(3)	111.5(4)	106.8(7)
H(*n*1A)–C(*n*1)–H(*n*1B)	108.9(5)	108.5(4)	112.1(8)	110.2(8)
H(*n*1A)–C(*n*1)–C(*n*2)	112.1(5)	110.6(4)	111.3(6)	115.8(7)
H(*n*1B)–C(*n*1)–C(*n*2)	109.9(5)	111.8(5)	111.1(5)	103.4(7)
N(*n*)–C(*n*1)–H(*n*1A)	111.5(4)	108.4(5)	110.8(6)	111.9(8)
N(*n*)–C(*n*1)–H(*n*1B)	107.6(4)	111.2(5)	109.6(5)	108.6(7)
H(*n*2A)–C(*n*2)–H(*n*2B)	108.1(5)	108.9(7)	108.7(8)	111.6(8)
C(*n*1)–C(*n*2)–H(*n*2A)	111.4(5)	110.1(4)	111.1(7)	111.9(7)
C(*n*1)–C(*n*2)–H(*n*2B)	110.2(6)	110.6(4)	109.9(5)	110.1(8)
O(*n*)–C(*n*2)–H(*n*2A)	109.8(5)	110.0(4)	109.1(5)	106.1(8)
O(*n*)–C(*n*2)–H(*n*2B)	109.3(5)	109.6(4)	111.2(7)	108.9(7)

(*b*) Anions

Cl(1)–O(41)	1.408(5)	Cl(2)–O(51)	1.451(6)
Cl(1)–O(42)	1.403(4)	Cl(2)–O(52)	1.430(5)
Cl(1)–O(43)	1.373(11)	Cl(2)–O(53)	1.439(6)
Cl(1)–O(44)	1.390(12)	Cl(2)–O(54)	1.433(5)
O(41)–Cl(1)–O(42)	112.6(3)	O(51)–Cl(2)–O(52)	110.3(4)
O(41)–Cl(1)–O(43)	108.3(5)	O(51)–Cl(2)–O(53)	108.9(3)
O(41)–Cl(1)–O(44)	108.4(6)	O(51)–Cl(2)–O(54)	109.8(4)
O(42)–Cl(1)–O(43)	110.6(4)	O(52)–Cl(2)–O(53)	109.0(4)
O(42)–Cl(1)–O(44)	106.3(6)	O(52)–Cl(2)–O(54)	109.9(3)
O(43)–Cl(1)–O(44)	110.7(7)	O(53)–Cl(2)–O(54)	109.0(4)

$[NO_3]_2$,[4] calculations of the least-squares planes showed that the same ligand planarity exists, and that all atoms lie within 0.05 Å of the plane, apart from the carbon alpha to nitrogen.

Now if only the atoms N,C,C,O are considered, in each case the atoms are arranged in a *gauche* configuration and, for a fully ordered model, the configuration may be represented as Λδδλ or Δλλδ, since each cation (but not the crystal, owing to the centrosymmetry) is optically active. Our results, however, show the existence of 23(1)% Λδλλ. Furthermore, it is to be noted that for the statistical possibility in which the monomer containing ring 3A is linked through hydrogen bonding to the monomer containing ring 3C, the two-fold axis operates only at the crystal level, not at a molecular level.

According to Corey and Bailar,[16] these are not the most stable configurations for tris(ethylenediamine)cobalt(III) complexes, but Ibers and co-workers[17] have shown, using *X*-ray crystallographic evidence, that hydrogen bonding may change the relative stabilities of the configurations. The hydrogen bonds from the water oxygen to the ring-3 nitrogen are short. Since the site-occupancy factor of the Λδλλ configuration, 0.23(1), and that of the disordered water molecule, 0.25(1), are practically identical, it is likely that this particular configuration is stabilised by these hydrogen bonds.

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