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Synthesis, structure and spectroscopic studies on hydroxo-bridged heterotrinuclear complexes of cobalt(III) with ethane-1,2-diamine and ammonia as terminal ligands†

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Hydroxo-bridged homo- and hetero-trinuclear cobalt(III) complexes of the type $[M^{II}(H_2O)_2\{(OH)_2Co^{III}(N_4)\}_2]X_2\cdot nH_2O$ [M^{II} = a divalent metal ion such as Co^{II}, Ni^{II} or Zn^{II}; N_4 = $(en)_2$ (en = ethane-1,2-diamine) or $(NH_3)_4$; X = SO_4 or $(ClO_4)_2$; n = 3 or 5] have been prepared and spectroscopically characterized. The structure of $[Cu\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot 2H_2O$ **1** has been determined. The geometry around copper atom is a pseudo-square-based pyramid, with the basal sites occupied by four bridging hydroxide oxygens and the apical site is occupied by a weakly co-ordinated sulfate anion [Cu–O 2.516(4) Å]. The hydroxo groups bridge pairs of cobalt(III) ions which are in near-octahedral environments. The ethylenediamine chelate rings have the twist conformation. In the crystal structure of $[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4\cdot 2H_2O$ **2** the perchlorate ion is not co-ordinated and the en ligands have 'envelope' conformations. The sulfate ion in $[Cu\{(OH)_2Co(NH_3)_4\}_2][SO_4]_2\cdot 4H_2O$ **3** is not co-ordinated to the central copper ion. Electronic, infrared and variable-temperature EPR spectral data are discussed.

There has been a tremendous upsurge of interest in homo- and hetero-polynuclear complexes[1] due to their importance in the study of magnetic exchange interactions, electron transfer between metal ions, and as models for biological systems. New magnetic exchange pathways can be expected for hetero di- and tri-nuclear complexes where different sets of magnetic orbitals could be brought into close proximity. Investigations on such complexes could therefore be more informative in comparison to those on homo di- and tri-nuclear complexes. However, there have been few studies on heteropolynuclear complexes with different paramagnetic centres and these are limited to a small number of known and fully characterized compounds, possibly owing to the difficulties in synthesis.[1] Further, work on compounds of the 3d series is scanty when compared to those of the 4d and 5d series.

Polynuclear complexes with hydroxide as bridging ligand exhibit rather interesting chemistry and are relevant to applied chemistry and biology. Those of cobalt(III) and chromium(III) can be isolated as well defined crystalline solids. However, structural studies on polynuclear cobalt(III) hydroxo complexes are scarce when compared to those on chromium(III) complexes. As noted by Springborg[1] in his review on hydroxo-bridged complexes of trivalent Cr, Co, Rh and Ir, most singly bridged hydroxo complexes are of Cr^{III} and no structural study has been made for analogous cobalt(III) complexes. Further, in binuclear hydroxo-bridged ethane-1,2-diamine (en) complexes both *meso* and racemic forms have been reported for Cr^{III} but only the *meso* form is known for Co^{III}. A series of trinuclear complexes of the type $[M^{II}(H_2O)_2\{(OH)_2Cr^{III}(N_4)\}_2]^{4+}$ [M^{II} = Zn^{II}, Cu^{II} or Mn^{II}; N_4 (2-pyridylmethyl)amine, *N*,*N*′-bis(2-pyridylmethyl)propane-1,3-diamine, or 1,4,8,11-tetraazacyclotetradecane] have been investigated by Hodgson and co-workers.[2–4] Only the magnetic properties of the complexes of the type $[M^{II}(H_2O)_2\{(OH)_2Co^{III}(en)_2\}_2]^{4+}$ (M^{II} = Ni^{II} or Co^{II}) have been studied by Kobayashi *et al.*[5] Among the tri- and tetra-nuclear complexes, cobalt(III) complexes are structurally the least characterized and the studies are mainly confined to solution. Although a linear hydroxo-bridged trinuclear complex of cobalt(III) is known from Werner's time, its structure has not been determined.[6]

We report here the synthesis, crystal structure and spectral characterization of some hydroxo-bridged homo- and hetero-trinuclear cobalt(III) complexes with en and ammonia as terminal ligands. The structures of $[Cu\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot 2H_2O$ **1**, $[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4\cdot 2H_2O$ **2** and $[Cu\{(OH)_2Co(NH_3)_4\}_2][SO_4]_2\cdot 4H_2O$ **3** have been determined. A comparison is made with structurally related compounds.

Experimental

Reagents

The metal salts employed were BDH reagent-grade chemicals. The salt $Cu(ClO_4)_2\cdot 6H_2O$ was prepared by dissolving copper(II) oxide or carbonate in 10% perchloric acid. The solution was filtered and evaporated on a water-bath and the concentrated solution was kept over fused $CaCl_2$ *in vacuo* when crystals of $Cu(ClO_4)_2\cdot 6H_2O$ were obtained. Ammonia liquor was a Ranbauxy product (sp. gr. 0.91). Ethane-1,2-diamine (BDH) was distilled before use. The starting materials $[Co(en)_2(CO_3)]Cl\cdot H_2O$ and $[Co(NH_3)_4(CO_3)]Cl$ were prepared according to the literature methods,[7,8] $[Co(en)_2(CO_3)]ClO_4$ by adding a saturated aqueous solution of $NaClO_4\cdot H_2O$ to a cold aqueous solution of $[Co(en)_2(CO_3)]Cl\cdot H_2O$.

Syntheses

$[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot 5H_2O$. To $[Co(en)_2(CO_3)]Cl\cdot H_2O$ (4 g, 0.0137 mol) in water (10 cm^3) were added 1 mol dm^{-3} H_2SO_4 (20 cm^3), Na_2SO_4 (2 g, 0.014 mol) and $CoSO_4\cdot 7H_2O$ (1.7 g, 0.006 mol) with stirring until the evolution of CO_2 ceased and a clear red solution was obtained. Dilute NaOH (0.1 mol dm^{-3}) was then added dropwise with stirring until the appearance of turbidity. Stirring was continued for 2 h and the pale pink precipitate obtained was filtered off, washed with water, alcohol and diethyl ether and dried in air. Yield 1.84 g (38%) (Found: C, 11.05; H, 5.65; Co, 21.5; N, 13.1. Calc. for $[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot 5H_2O$: C, 11.15; H, 6.30; Co, 22.0; N, 13.35%).

$[Ni(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot 3H_2O$. The above procedure was followed using $NiSO_4\cdot 7H_2O$ (1.5 g, 0.006 mol). The compound is pale pink. Yield 1.62 g (35%) (Found: C, 12.35; H,

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† *Non-SI unit employed:* G = 10^{-4} T.

5.60; Co, 15.25; N, 14.5; Ni, 7.50. Calc. for $[Ni(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot3H_2O$: C, 12.55; H, 6.00; Co, 15.4; N, 14.6; Ni, 7.65%).

$[Cu\{(OH)_2Co(en)_2\}_2][SO_4]_2$. The complex $[Co(en)_2(CO_3)]Cl\cdot H_2O$ (0.0137 mol) was dissolved in water (10 cm^3), 1 mol dm^{-3} H_2SO_4 (20 cm^3) and Na_2SO_4 (2 g, 0.014 mol) were added and stirred. Stirring was continued until the evolution of CO_2 ceased. The compound $CuSO_4\cdot5H_2O$ (1.5 g, 0.006 mol) was added with stirring. 0.1 mol dm^{-3} Sodium hydroxide was then added dropwise with stirring when a pale pink precipitate separated. Stirring was continued for 2 h to complete the reaction. The product was purified and dried in air. Yield 1.68 g (41%) (Found: C, 13.3; H, 5.60; Co, 16.05; Cu, 8.20; N, 15.65. Calc. for $[Cu\{(OH)_2Co(en)_2\}_2][SO_4]_2$: C, 12.75; H, 5.30; Co, 15.65; Cu, 8.40; N, 14.85%).

$[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4\cdot2H_2O$. To $[Co(en)_2(CO_3)]Cl\cdot H_2O$ (2 g) were added 2 mol dm^{-3} perchloric acid (10 cm^3), $NaClO_4\cdot H_2O$ (2 g, 0.014 mol) and $Cu(ClO_4)_2\cdot6H_2O$ (1.8 g, 0.005 mol). The mixture was stirred until the evolution of CO_2 ceased and a clear red solution obtained. The pH was then raised to about 9 by adding 0.1 mol dm^{-3} NaOH and left in a beaker. After 2 d a red crystalline product deposited at the bottom of the beaker. It was purified and dried as before. Yield 1.85 g (40%) (Found: C, 10.1; H, 4.00; Co, 12.7; Cu, 6.70; N, 12.2. Calc. for $[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4\cdot2H_2O$: C, 10.4; H, 4.35; Co, 12.75; Cu, 6.90; N, 12.15%).

CAUTION: perchlorate salts are potentially explosive and should be handled with care and in small quantities under appropriate safety conditions.

$[Zn(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot5H_2O$. To $[Co(en)_2(CO_3)]Cl\cdot H_2O$ (4 g, 0.0136 mol) in water (20 cm^3) were added 1 mol dm^{-3} H_2SO_4 (10 cm^3), Na_2SO_4 (2.5 g) and $ZnSO_4\cdot7H_2O$ (0.9 g, 0.006 mol) with stirring. The pH was raised by adding 0.1 mol dm^{-3} NaOH. Near pH 7 a pale pink silky precipitate separated. Stirring was continued for 1 h. Then the solid was filtered off, purified and dried in air. Yield 1.94 g (40%) (Found: C, 11.7; H, 5.60; Co, 15.0; N, 13.6; Zn, 8.25. Calc. for $[Zn(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot H_2O$: C, 11.85; H, 6.20; Co, 14.55; N, 13.85; Zn, 8.05%).

$[Cu\{(OH)_2Co(NH_3)_4\}_2][SO_4]_2\cdot4H_2O$. The complex $[Co(NH_3)_4(CO_3)]Cl$ (2.30 g, 0.01 mol) was dissolved in water (10 cm^3), 1 mol dm^{-3} H_2SO_4 (20 cm^3) and Na_2SO_4 (2.5 g, 0.018 mol) were then added and the mixture was stirred for 5 min. The salt $CuSO_4\cdot5H_2O$ (1.2 g, 0.005 mol) was added and stirring continued until a clear red solution was obtained. The pH was then slowly increased to about 6 by adding 0.1 mol dm^{-3} NaOH with stirring. Stirring was continued for 0.5 h, when a pale pink solid precipitated. The product was purified and dried. Yield 1.17 g (36%) (Found: H, 5.30; Co, 18.2; Cu, 9.65; N, 17.2. Calc. for $[Cu\{(OH)_2Cu(NH_3)_4\}_2][SO_4]_2\cdot4H_2O$: H, 5.60; Co, 18.15; Cu, 9.80; N, 17.25%).

$[Ni(H_2O)_2\{(OH)_2Co(NH_3)_4\}][SO_4]_2\cdot5H_2O$. This complex was prepared by following the method given for the analogous copper complex using $NiSO_4\cdot7H_2O$ (1.5 g, 0.006 mol). Yield 1.68 g (40%) (Found: H, 5.50; Co, 16.65; N, 15.9; Ni, 8.25. Calc. for $[Ni(H_2O)_2\{(OH)_2Co(NH_3)_4\}_2][SO_4]_2\cdot5H_2O$: H, 6.00; Co, 16.85; N, 16.05; Ni, 8.4%).

Measurements

Electronic absorption spectra for solid and solution samples were recorded on a Hitachi U3400 spectrophotometer (solids as Nujol mulls), diffuse-reflectance spectra in the visible region on a Philips Scientific SP8-100 UV/VIS spectrophotometer using MgO as the standard. The solubility of the complexes in water is poor and saturated solutions were employed for measurements. Infrared spectra were recorded on an FT-IR Digilab (Bio-Rad) FTS 7 spectrometer in the range 4000–250 cm^{-1} using CsI windows by the mull technique and as high-density polyethylene pellets in the range 700–225 cm^{-1}. Electron paramagnetic resonance spectra of polycrystalline samples were measured on a Varian E-109 EPR X-band spectrometer at ambient (298 K) and liquid-nitrogen temperatures, using diphenylpicrylhydrazyl as an external standard. Metal analyses were performed on a Perkin-Elmer 2380 atomic absorption spectrophotometer. Microanalyses for carbon, hydrogen and nitrogen were done using a Helareus CHNO-Rapid Analyser.

X-Ray crystallography

Complex **1** crystallizes as reddish brown needles from the mother-liquor. Red plate-like crystals of **2** were obtained by a slow evaporation of an aqueous solution. Needle-like (prismatic) crystals of **3** were obtained by slow evaporation of a concentrated solution of the complex in the presence of sodium perchlorate.

Data for all three crystals were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature. The unit-cell parameters were refined using 25 reflections. Three intensity-control reflections monitored every 3600 s of exposure time showed no decay. The data were corrected for Lorentz-polarization effects. An absorption correction was applied according to the method of North *et al.*[9] The structures were solved by the Patterson heavy-atom method and subsequent Fourier-difference syntheses using the SHELX system of programs.[10,11] Refinements (on *F*) were performed by the full-matrix least-squares method first with isotropic and subsequently with anisotropic thermal parameters for non-hydrogen atoms. The scattering factors used were as in the program; for Cu and Co they were taken from ref. 12. Anomalous dispersion corrections were applied for all the non-hydrogen atoms. Most hydrogen atoms were located from a Fourier-difference map and refined isotropically. The rest were fixed at geometrically calculated positions and included in the structure-factor calculations with thermal parameters set equal to 0.05 $Å^2$. A weighting scheme based on counting statistics was applied. The program ORTEP[13] was used for drawing structural diagrams. The crystallographic data and experimental details are summarized in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/99.

Results and Discussion

Structure of $[Cu\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot2H_2O$ 1

An ORTEP diagram of complex **1** with the atom labelling scheme is shown in Fig. 1 and selected bond distances and angles in Table 2. The co-ordination geometry around copper(II) can be best described as a pseudo-square-based pyramid with the basal sites occupied by four bridging hydroxide oxygens. At the apical site the oxygen atom O(22) of the sulfate anion is weakly co-ordinated with a Cu–O distance of 2.516(4) Å. This distance is much greater than that in the equatorial plane and such an elongated axial bond is a common feature of five-co-ordinated copper(II) complexes.[14–16] It is significantly greater than that found in other copper(II) complexes with monodentate sulfate groups[17 18] (1.9–2.2 Å). This suggests that the interaction between copper and the sulfate group may be best described by, as Hathaway and co-workers[19] have termed, 'semi-co-ordination', representing a weak covalent interaction. The hydroxo groups bridge two cobalt(III) ions in pairs which are in nearly octahedral environments. The intermetallic separations, Cu(1) • • • Co(1) 2.894(1) and Cu(1) • • • Co(2) 2.901(1) Å are slightly smaller than the Co • • • Co separations 2.93–2.97 Å found in di-μ-hydroxo-dicobalt(III) complexes.[1] The Cu–O bond lengths are asymmetric and comparable to those found in the other hydroxo-bridged copper(II) dimers,[20] but larger than those reported for copper(II)-dichromium(III) complexes.[21] The copper and the four oxygen atoms which describe the equatorial planes of the two octahedra are coplanar.

The eight Co–N distances lying in the range 1.924(4)–1.983(4) Å are comparable to those found in other binuclear hydroxo-bridged cobalt en complexes. The mean chelate bite angle (N–Co–N), 86.1(8)°, is smaller by *ca.* 4° than the expected 90° for a bis(chelate) octahedral co-ordination. The angle between Co–N bonds of adjacent chelate rings is larger than 90°. This effect is also noted for complex **2**. The conformation of ring 1, Co(1)–N(1)–C(1)–C(2)–N(2), is midway between an envelope and a twist conformation. Ring 2, Co(1)–N(3)–C(3)–C(4)–N(4), is puckered and adopts a twist conformation. Rings 3, Co(2)–N(5)–C(5)–C(6)–N(6), and 4, Co(2)–N(7)–C(7)–C(8)–N(8), also adopt twist conformations with the twist axis passing through Co(2). Each of the en rings is puckered in a chiral way. The designation of the cobalt(III) units $[Co(en)_2(OH)_2]^+$ in the complex cation shown in Fig. 1 are ${}^{\delta}{}_{\lambda}\Delta$ and $\Lambda^{\delta}{}_{\delta}$ for Co(1) and Co(2) respectively, where Δ and Λ represent the metal atom configurations while λ and δ denote the en ring conformations.[22] The conformation of en and the weak co-ordination of the sulfate anion render the cation optically active in the solid state, though the activity would be negligible. However, in aqueous solution the complex did not show any optical activity.

The complex cations, anions and water molecules are held together in the lattice through a network of inter- and intramolecular hydrogen bonds and van der Waals interactions.

Structure of $[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4\cdot2H_2O$ 2

An ORTEP view of complex **2** is shown in Fig. 2 together with the atom numbering scheme. Selected interatomic distances and angles are given in Table 3. The copper atom sits on a crystallographic inversion centre and is bonded to four oxygens of the hydroxo bridges defining a square plane. As in **1**, the hydroxo groups bridge the cobalt atoms on either side. Each cobalt atom is nearly in an octahedral environment formed by

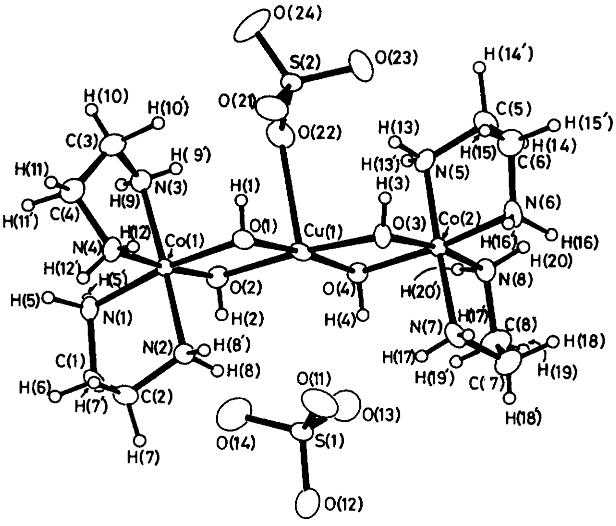

Fig. 1 An ORTEP view of $[Cu\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot2H_2O$ **1** with the atom numbering scheme

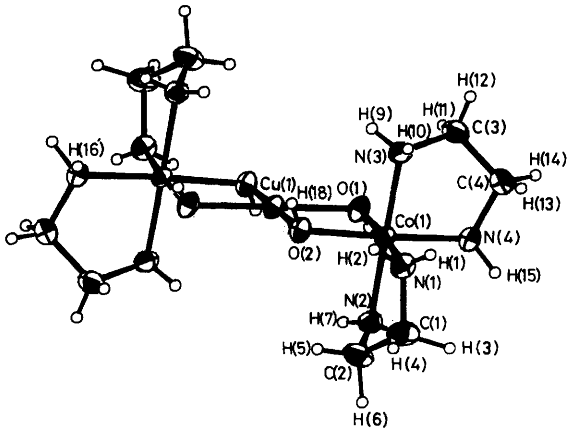

Fig. 2 An ORTEP view of the cationic complex $[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4\cdot2H_2O$ **2** with the atom numbering scheme

Table 1 Crystallographic data and experimental details *

	1	**2**	**3**
Formula	$C_8H_{40}Co_2CuN_8O_{14}S_2$	$C_8H_{40}Cl_4Co_2CuN_8O_{22}$	$H_{36}Co_2CuN_8O_{16}S_2$
M	717.98	923.69	649.88
Crystal size/mm	0.4 × 0.15 × 0.1	0.42 × 0.22 × 0.07	0.4 × 0.1 × 0.05
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/c$
a/Å	6.262(3)	7.909(1)	6.220(1)
b/Å	13.720(3)	8.049(2)	16.956(1)
c/Å	14.301(4)	12.473(2)	9.994(2)
α/°		79.50(1)	
β/°	101.46(3)	89.71(1)	95.44(1)
γ/°		80.60(1)	
U/Å^3	1204.2	770.0	1049.3
Z	2	1	2
D_c/g cm^{-3}	1.980	1.992	2.057
μ(Mo-Kα)/cm^{-1}	25.2	22	14.5
Transmission coefficient	0.8–0.98	0.82–0.98	0.8–0.98
g	0.000 359	0.001 623	0.0000
Total measured/unique reflections	2478	3594	2580
Observed reflections [$\lvert F_o\rvert \geqslant 5\sigma\lvert F_o\rvert$]	2157	3045	1855
Parameters defined	315	285	133
R	0.0271	0.0366	0.0425
R′	0.0300	0.0418	0.0495

* Details in common: λ(Mo-Kα) 0.710 69 Å; 21 °C; $R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$; $R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma\lvert F_o\rvert^2]^{\frac{1}{2}}$. $w = 1.00/[\sigma^2(F) + gF^2]$.

Table 2 Selected bond distances (Å) and angles (°) of complex **1**

Cu(1) ··· Co(1)	2.894(1)	Cu(1) ··· Co(2)	2.901(1)
Cu(1)–O(1)	1.954(3)	Cu(1)–O(2)	1.974(4)
Cu(1)–O(3)	1.923(4)	Cu(1)–O(4)	1.960(3)
Cu(1)–O(22)	2.516(4)	Co(1)–O(1)	1.898(4)
Co(1)–O(2)	1.912(3)	Co(1)–N(1)	1.983(4)
Co(1)–N(2)	1.937(4)	Co(1)–N(3)	1.955(4)
Co(1)–N(4)	1.948(5)	Co(2)–O(3)	1.919(4)
Co(2)–O(4)	1.932(4)	Co(2)–N(5)	1.936(4)
Co(2)–N(6)	1.924(4)	Co(2)–N(7)	1.967(4)
Co(2)–N(8)	1.948(5)		
Cu(1)–O(1)–Co(1)	97.4(2)	Cu(1)–O(2)–Co(1)	96.3(2)
Cu(1)–O(3)–Co(2)	98.0(2)	Cu(1)–O(4)–Co(2)	96.4(2)
O(1)–Cu(1)–O(2)	81.6(2)	O(1)–Cu(1)–O(3)	98.6(2)
O(1)–Cu(1)–O(4)	175.0(1)	O(2)–Cu(1)–O(3)	174.8(1)
O(2)–Cu(1)–O(4)	97.3(2)	O(3)–Cu(1)–O(4)	82.1(2)
Co(1)–Cu(1)–Co(2)	175.1(0)	O(1)–Cu(1)–O(22)	85.4(1)
O(2)–Cu(1)–O(22)	91.4(1)	O(3)–Cu(1)–O(22)	93.9(1)
O(4)–Cu(1)–O(22)	99.6(1)	O(1)–Co(1)–O(2)	84.7(2)
O(1)–Co(1)–N(1)	172.3(2)	O(1)–Co(1)–N(2)	88.5(2)
O(1)–Co(1)–N(3)	93.6(2)	O(1)–Co(1)–N(4)	93.3(2)
O(2)–Co(1)–N(1)	91.3(2)	O(2)–Co(1)–N(2)	93.0(2)
O(2)–Co(1)–N(3)	89.0(2)	O(2)–Co(1)–N(4)	174.2(2)
N(1)–Co(1)–N(2)	85.2(2)	N(1)–Co(1)–N(3)	92.9(2)
N(1)–Co(1)–N(4)	91.3(2)	N(2)–Co(1)–N(3)	177.3(2)
N(2)–Co(1)–N(4)	92.3(2)	N(3)–Co(1)–N(4)	85.8(2)
O(3)–Co(2)–O(4)	82.9(2)	O(3)–Co(2)–N(5)	94.1(2)
O(3)–Co(2)–N(6)	93.1(2)	O(3)–Co(2)–N(7)	88.8(2)
O(3)–Co(2)–N(8)	170.9(2)	O(4)–Co(2)–N(5)	88.6(2)
O(4)–Co(2)–N(6)	173.9(2)	O(4)–Co(2)–N(7)	92.3(2)
O(4)–Co(2)–N(8)	89.6(2)	N(5)–Co(2)–N(6)	87.0(2)
N(5)–Co(2)–N(7)	177.1(2)	N(5)–Co(2)–N(8)	90.8(2)
N(6)–Co(2)–N(7)	92.3(2)	N(6)–Co(2)–N(8)	94.8(2)
N(7)–Co(2)–N(8)	86.4(2)	Cu(1)–O(22)–S(2)	122.3(2)

Table 3 Selected bond distances (Å) and angles (°) of complex **2**

Cu(1) ··· Co(1)	2.899(1)	Cu(1)–O(1)	1.909(1)
Cu(1)–O(2)	1.948(1)	Co(1)–O(1)	1.906(1)
Co(1)–O(2)	1.905(1)	Co(1)–N(1)	1.956(2)
Co(1)–N(2)	1.957(2)	Co(1)–N(3)	1.949(2)
Co(1)–N(4)	1.951(2)		
Cu(1)–O(1)–Co(1)	98.9(1)	Cu(1)–O(2)–Co(1)	97.61(1)
O(1)–Cu(1)–O(2)	81.1(1)	O(1)–Co(1)–O(2)	82.3(1)
Co(1)–N(1)–C(1)	110.4(2)	Co(1)–N(2)–C(2)	108.6(2)
Co(1)–N(3)–C(3)	108.8(2)	Co(1)–N(4)–C(4)	110.5(2)
O(1)–Co(1)–N(1)	174.2(1)	O(1)–Co(1)–N(2)	93.2(1)
O(1)–Co(1)–N(3)	87.7(1)	O(1)–Co(1)–N(4)	91.8(1)
O(2)–Co(1)–N(1)	92.0(1)	O(2)–Co(1)–N(2)	88.0(1)
O(2)–Co(1)–N(3)	92.8(1)	O(2)–Co(1)–N(4)	173.9(1)
N(1)–Co(1)–N(2)	85.6(1)	N(1)–Co(1)–N(3)	93.6(1)
N(1)–Co(1)–N(4)	94.0(1)	N(2)–Co(1)–N(3)	178.9(1)
N(2)–Co(1)–N(4)	93.4(1)	N(3)–Co(1)–N(4)	85.9(1)

two oxygen atoms from the hydroxo groups and four nitrogen atoms from en ligands.

The Cu–O bond lengths, 1.909(1) and 1.948(1) Å, are asymmetric and the mean value is significantly shorter than that in complex **1**. The Co–O distances are symmetric and are again shorter than those in **1**. However the Cu ··· Co separation 2.899(0) Å agrees well with that of **1**. The equatorial plane of the cobalt octahedron defined by the five atoms is coplanar. The en ring 1, Co(1)–N(1)–C(1)–C(2)–N(2), adopts an envelope conformation with apex at C(2). Ring 2, Co(1)–N(3)–C(3)–C(4)–N(4), also adopts an envelope conformation with apex at C(3). The general configuration and conformation around cobalt can be denoted by the symbols ${}^{\lambda}_{\lambda}\Lambda$ and Δ^{δ}_{δ}. Thus, the complex cation is an optically inactive mesoform owing to the presence of the inversion centre at Cu. The molecules in the unit cell are held by O–H ··· O intramolecular hydrogen bonds.

Table 4 Selected bond distances (Å) and angles (°) of complex **3**

Cu(1) ··· Co(1)	2.888(1)	Cu(1)–O(1)	1.926(3)
Cu(1)–O(2)	1.946(3)	Co(1)–O(1)	1.918(3)
Co(1)–O(2)	1.923(3)	Co(1)–N(1)	1.952(4)
Co(1)–N(2)	1.961(3)	Co(1)–N(3)	1.947(3)
Co(1)–N(4)	1.949(4)		
O(1)–Cu(1)–O(2)	82.2(1)	O(1)–Co(1)–O(2)	83.0(1)
Cu(1)–O(1)–Co(1)	97.4(2)	Cu(1)–O(2)–Co(1)	96.6(1)
O(1)–Co(1)–N(1)	176.1(1)	O(1)–Co(1)–N(2)	89.0(2)
O(1)–Co(1)–N(3)	91.1(2)	O(1)–Co(1)–N(4)	92.3(2)
O(2)–Co(1)–N(1)	93.3(2)	O(2)–Co(1)–N(2)	92.8(1)
O(2)–Co(1)–N(3)	173.2(2)	O(2)–Co(1)–N(4)	86.2(2)
N(1)–Co(1)–N(2)	89.8(2)	N(1)–Co(1)–N(3)	92.6(2)
N(1)–Co(1)–N(4)	88.8(2)	N(2)–Co(1)–N(3)	90.6(2)
N(2)–Co(1)–N(4)	178.2(2)	N(3)–Co(1)–N(4)	90.7(2)

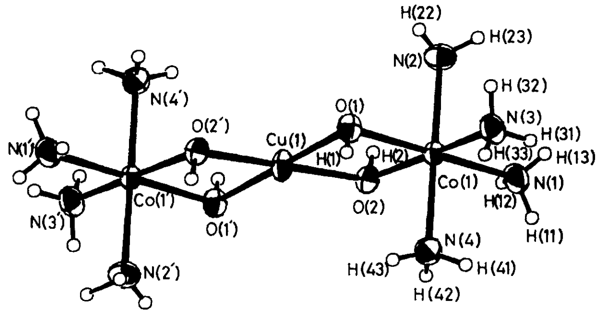

Fig. 3 An ORTEP view of the cationic complex $[Cu\{(OH)_2Co(NH_3)_4\}_2][SO_4]_2 \cdot 4H_2O$ **3** with the atom numbering scheme

Structure of $[Cu\{(OH)_2Co(NH_3)_4\}_2][SO_4]_2 \cdot 4H_2O$ 3

The structure of complex **3** with the atom labelling scheme is shown in Fig. 3. Selected bond lengths and angles in Table 4. As in **2**, the copper ion is placed on a crystallographic inversion centre. The geometry at the cobalt is a near octahedron with the other four positions occupied by NH_3 ligands. The Cu–O bond lengths are asymmetric and lie between those of complexes **1** and **2**. The Co–O distances, 1.918(3) and 1.923(3) Å, are symmetric and are comparable to those of **1** and cobalt is in a near-octahedral environment. The Co–N distances are symmetric and comparable to those found in **1** and **2**. The molecule is packed in the lattice with a three-dimensional network of hydrogen bonds and van der Waals interactions.

In complex **1** the SO_4 ion is involved in a network of inter- and intra-molecular hydrogen bonds while in the ClO_4 ion in **2** only one oxygen is involved in an intramolecular hydrogen bond.

Spectroscopic studies

Electronic spectra. The electronic spectral data for the trinuclear complexes investigated are compared with those of analogous mono-, di- and tetra-meric complexes in Table 5. The observed spectra are mainly dominated by the low-spin cobalt(III) transitions of the octahedral geometry in the visible region obscuring the transitions of the divalent metal ion. The spectrum of complex **2** is shown in Fig. 4. For $[Co(en)_2(OH)_2]^+$ units of bi, tri- and tetra-nuclear complexes, the observed v_1 band compares well with the mean value of the first two transitions,[23] 18 200 and 22 500 cm^{-1}, of *trans*-$[Co(en)_2(H_2O)_2]^{3+}$ (OH^- and H_2O occupy positions near to each other in the spectrochemical series). By approximating the Racah interelectron repulsion parameter *C* as 4*B* for a strong-field complex, the ligand-field parameters 10 *Dq* and *B* were calculated, and are consistent with those of related mono-, bi- and tetra-nuclear complexes[24,27–29] listed in Table 5. The values of 10 *Dq* and *B'* of octahedral Co^{III} in $[Co(en)_2(OH)_2]^+$

Table 5 Electronic spectral data (cm^{-1}) for octahedral Co^{III} in mono-, di-, tri- and tetra-nuclear complexes

Complex	$^1T_{1g} \longleftarrow {}^1A_{1g}$	$^1T_{2g} \longleftarrow {}^1A_{1g}$	$10Dq$/cm^{-1}	B'/cm^{-1}	$\beta = B'/B^0$
$[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2 \cdot 5H_2O$	19 620	28 490	20 405	671	0.61
$[Ni(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2 \cdot 3H_2O$	19 540	28 010	20 375	633	0.58
$[Cu\{(OH)_2Co(en)_2\}][SO_4]_2 \cdot 2H_2O$	19 520	28 090	20 350	642	0.58
$[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4 \cdot 2H_2O$	19 850	28 920	20 616	688	0.63
$[Zn(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2 \cdot 5H_2O$	19 650	27 890	20 530	611	0.56
$[Cu\{(OH)_2Co(NH_3)_4\}_2][SO_4]_2 \cdot 4H_2O$	19 800	27 780	20 719	585	0.53
$[Ni(H_2O)_2\{(OH)_2Co(NH_3)_4\}][SO_4]_2 \cdot 5H_2O$	19 610	27 030	20 546	538	0.49
$[(en)_2Co(OH)_2Co(en)_2]^{4+}$[25]	18 800	26 670	19 637	583	0.53
$[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4+}$[26]	18 940	27 030	19 770	602	0.55
$[Co\{(OH)_2Co(en)_2\}_3]^{6+}$[23]	20 410	33 000	23 557	787	0.72
$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$[24]	20 280	33 110	23 491	802	0.73
$[Co(en)_2(OH)_2]^{+}$[2]	19 340	26 950	20 251	556	0.51

* $B^0 = 1100$ cm^{-1} for free cobalt(III) ion.

Table 6 The EPR parameters for complexes **1**–**3**

	Single crystals			Polycrystalline		
Complex	$g_\parallel$	$10^4A_\parallel$/cm^{-1}	$g_\perp$	$g_\parallel$	$10^4A_\parallel$/cm^{-1}	$g_\perp$
1	2.293	161	2.052	2.342	164	2.063
2	2.317	—	2.061	2.357	—	2.069
3	2.293		2.053	2.269	—	2.053

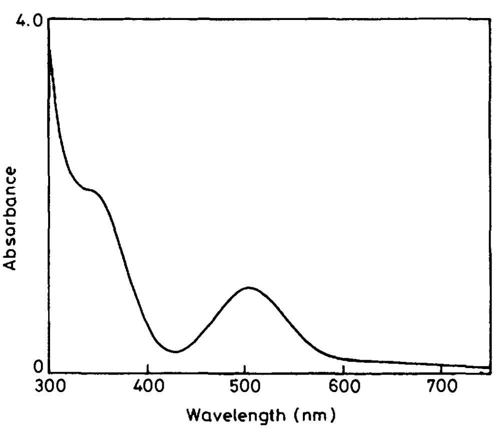

Fig. 4 Electronic absorption spectrum of $[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4 \cdot 2H_2O$ in aqueous solution

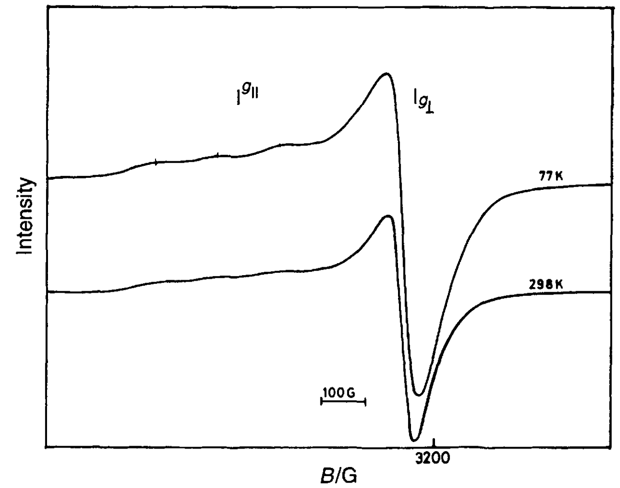

Fig. 5 The EPR spectra of $[Cu\{(OH)_2Co(en)_2\}_2][SO_4]_2 \cdot 2H_2O$ **1** as a powdered sample diluted with the diamagnetic host $[Zn(H_2O)\{(OH)_2Co(en)_2\}_2][SO_4]_2 \cdot 5H_2O$ at two temperatures

increase with increase in nuclearity. For example, B' lies in the ranges 550–600, 610–670 and 780–800 cm^{-1} for bi-, tri- and tetra-nuclear complexes respectively. Table 5 also lists the β values which may be taken as a measure of the covalency of the metal–ligand bond.

Infrared spectra. The infrared spectra of hydroxo-bridged trinuclear transition-metal complexes have not been well investigated, although studies on related binuclear complexes have been made. In the region of the OH and NH_2 stretching modes the highest frequencies are observed for the perchlorate complex as expected since the perchlorate anion does not take part in hydrogen bonding. The occurrence of more than two main bands in the NH stretching region for some complexes is due to hydrogen-bonded and free NH_2 groups. The infrared spectra of the complexes show the same general pattern for the en bands. Hence these chelate rings may have the same *gauche* configuration, which is typical for the en chelate ring. A feature of the spectra is a strong absorption near 495–515 cm^{-1} assignable to the metal–oxygen stretching mode. On the basis of D_{2h} symmetry for the bridge unit, $Cu(OH)_2Co$, two modes, asymmetric and symmetric, for the metal–oxygen stretching vibrations should be infrared active and all the hydroxo-bridged complexes show these characteristic absorptions. For hydroxo-bridged binuclear complexes of copper a band at 480–515 cm^{-1} has been assigned to Cu–O stretching,[30] which is metal sensitive. Bands of weak to medium intensity observed near 1010 cm^{-1} for the trinuclear complexes investigated are due to OH bending vibrations.[31]

EPR spectra. The cobalt complex, $[Co(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2 \cdot 5H_2O$ does not give any EPR spectrum at room temperature. However, at 77 K it shows a broad peak of linewidth nearly 525 G. The g value was found to be 5.31. This high g value indicates that the central Co^{2+} ion is in an axially distorted (tetragonal or rhombic) octahedral geometry. For a d^7 ion in an octahedral field the predicted g value is 4.3. In distorted-octahedral fields both spin–orbit coupling and non-octahedral crystal fields lead to markedly different g components. The spectra of the nickel complexes are broad and featureless even at liquid-nitrogen temperature. Fig. 5 shows the EPR spectrum of a powdered sample of complex **1** diluted with the corresponding diamagnetic zinc complex. The single crystals give a similar spectrum. It consists of well resolved and easily identifiable parallel components of the hyperfine splitting (the fourth component seems to have merged

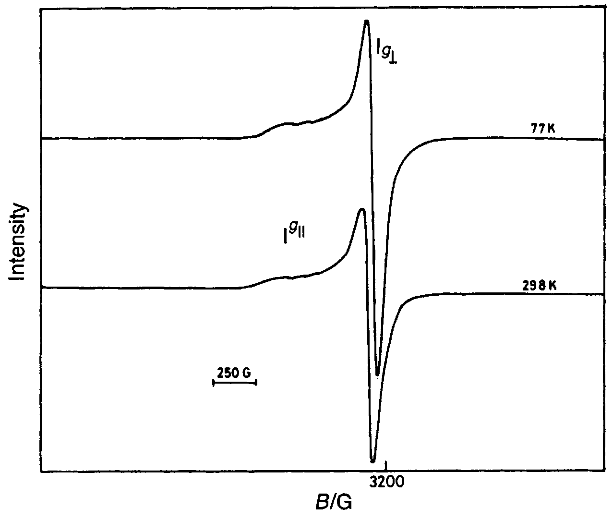

Fig. 6 The EPR spectra of $[Cu\{(OH)_2Co(en)_2\}_2][ClO_4]_4\cdot 2H_2O$ **2** as a powdered sample diluted with diamagnetic $[Zn(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot 5H_2O$ at two temperatures

with the strong absorption in the $g_\perp$ region). The perpendicular components are not resolved. The appearance of metal hyperfine splittings could be attributed to the considerable decrease in dipolar interactions of the copper(II) centres. The ambient and low-temperature (77 K) spectra are also similar except for the increase in signal intensity at low temperature. The observed $g_\parallel$ and $g_\perp$ for the copper(II) complexes are in accord with the $d_{x^2-y^2}$ orbital as the ground state. For copper(II) complexes $g_\parallel$ is a moderately sensitive function of covalency. For covalent complexes, $g_\parallel$ is normally less than 2.3, and for ionic environments values of $\geqslant 2.3$ have been observed. The $g_\parallel$ values given in Table 6 hence indicate an ionic environment for the copper(II) centres. Poorly resolved hyperfine lines were also observed for the perchlorate complex **2** and Fig. 6 shows a typical spectrum of the magnetically dilute species. Interestingly, the analogous ammine complex **3** does not show any hyperfine splitting. Only the Zeeman splitting corresponding to $g_\parallel$ and $g_\perp$ were resolved (Table 6). Even at 77 K, no hyperfine lines due to ^{63,65}Cu were observed (see Fig. 7). Therefore the dipolar interactions between the copper centres will be higher in the complexes **2** and **3** than in **1**. A larger Cu • • • Cu separation in **2** apparently results in the observed unresolved hyperfine splitting.

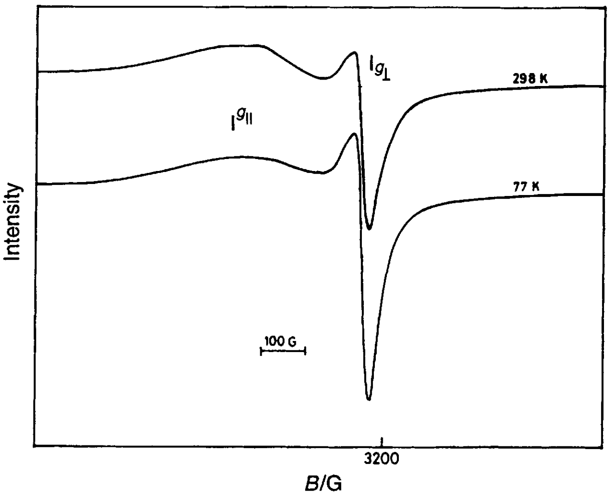

Fig. 7 The EPR spectra of $[Cu\{(OH)_2Co(NH_3)_4\}_2][SO_4]_2\cdot 4H_2O$ **3** as a powdered sample diluted with $[Zn(H_2O)_2\{(OH)_2Co(en)_2\}_2][SO_4]_2\cdot 5H_2O$ at two temperatures

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