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Cobalt(II) Complexes of 6-Methyl-2-oxypyridine (mhp): Crystal Structure of $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$

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$Co(mhp)_2$ and $Co(mhp)_2(bpy)$ (Hmhp = 6-methyl-2-hydroxypyridine, bpy = 2,2′-bipyridyl) have been prepared, and these complexes appear to be essentially monomeric. The molecular duodecanuclear cobalt(II) complex $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$ has been characterized crystallographically. It crystallizes together with disordered toluene molecules in space group $P\bar{3}$, with $a = 24.252$ (3) Å, $c = 16.859$ (3) Å, and $Z = 2$. The structure has been determined by direct methods from 4081 diffractometer data and refined to $R = 0.093$. The complex molecule, with an interior network of 12 cobalt atoms linked by bridging hydroxy, acetate, and mhp groups, has crystallographic C_3 symmetry and closely approximates to D_3 symmetry. Three of the Co atoms (two axial and one central) lie on the C_3 axis, three more lie in an equatorial plane, which contains the central cobalt atom and is perpendicular to the C_3 axis, and the other six ("tropical") Co atoms lie in two planes above and below the equatorial plane. These six "tropical" Co atoms form a distorted trigonal prism around the central Co atom, one triangular face being rotated by 19.9° with respect to the other; all five faces are capped by the axial and equatorial Co atoms. The central Co atom is coordinated by six μ_3-hydroxy groups, each of which is also bonded to one equatorial and one tropical Co atom; each acetate group bridges one equatorial and one tropical Co atom. Each of the twelve mhp ligands is bidentate, three to each of the two axial Co atoms, with the oxygen atom forming a bridge to a tropical Co atom, and one to each of the six tropical Co atoms, with the oxygen atom bridging to another tropical and to an equatorial Co atom. The Co···Co distances are all >3.1 Å, and the room-temperature magnetic moment of ca. 3.0 μ_B/Co atom is indicative of some magnetic exchange between the d^7 centers.

Introduction

The ability of the anion of 6-methyl-2-hydroxypyridine (Hmhp) to encourage the formation of dimeric metal complexes has been well demonstrated, particularly for the 4d transition metals Mo,[2] Ru,[3] Rh,[4] and Pd.[5] Apart from the initial report of $Cr_2(mhp)_4$[2] and the recent investigations leading to the isolation of $Cu_4(mhp)_4$[6] and $Cr_4(mhp)_8(OH)_4$,[7] complexes of this ligand with the 3d transition metals have not been described. Therefore, we have investigated the reactions of mhp with compounds of Fe(II), Ni(II), Co(II), and Zn(II), paying particular attention to the possibility of the formation of $M_2(mhp)_4$ complexes, as encountered with Cr(II), W(II),[2] and the 4d transition metals listed above. We have found these reactions to be diverse, and only in the case of Fe have we obtained any evidence for the formation of a simple dimer.[8] This paper describes some reactions between cobalt(II) acetate and Na(mhp) or Hmhp and the isolation and crystal structure of the novel complex $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$.

Experimental Section

Preparation of Bis(6-methyl-2-oxypyridine)cobalt(II), $Co(mhp)_2$. Cobalt(II) acetate (0.34 g, 1.92 mmol) and dry Na(mhp) (0.8 g, 6.1 mmol) were added to dry $CHCl_3$, and the mixture was stirred for 20 h, during which time the solution became blue-purple. The solution was filtered, and the solvent of the filtrate was removed under reduced pressure, to produce a blue-purple solid. Traces of solvent and some Hmhp were removed by pumping for 5–6 h at 150 °C. The material was recrystallized from dry toluene ($CHCl_3$ can also be used) and dried in vacuo (yield 0.42 g, 80%). Anal. Calcd for $Co(mhp)_2$, $C_{12}H_{12}N_2O_2Co$: C, 52.4; H, 4.4; N, 10.1; Co, 21.4. Found: C, 53.1; H, 4.9; N, 9.7; Co, 20.8.

$Co(mhp)_2$ is very sensitive to moisture, and exposure to air leads to the formation of Hmhp and a pale blue insoluble material. The compound is reasonably soluble in many of the common organic solvents.

Preparation of Bis(6-methyl-2-oxypyridine)(2,2′-bipyridyl)cobalt(II), $Co(mhp)_2(bpy)$. Bis(6-methyl-2-oxypyridine)cobalt(II), prepared as described above (0.3 g, 1.1 mmol), and 2,2′-bipyridyl (0.2 g, 1.26 mmol) were dissolved in methanol (10 cm^3), and the solution was stirred at room temperature for ca. 10 h. The precipitate that was formed was separated by filtration, washed with methanol (2 × 3 cm^3), and dried in vacuo. The product was recrystallized from CH_2Cl_2 (yield 0.33 g, 65%). Anal. Calcd for $Co(mhp)_2(bpy)$, $C_{22}H_{20}N_4O_2Co$: C, 61.2; H, 4.7; N, 13.0; Co, 13.7. Found: C, 60.8; H, 4.8; N, 12.9; Co, 13.8.

$Co(mhp)_2(bpy)$ is stable in air for several days. It is soluble in CH_2Cl_2 and $CHCl_3$, moderately soluble in methanol and ethanol, soluble in warm toluene, and insoluble in diethyl ether.

Preparation of $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$. Cobalt(II) acetate (0.4 g, 2.26 mmol) was heated at 120 °C in vacuo for ca. 2 h. 6-Methyl-2-hydroxypyridine (0.6 g, 5.50 mmol) was then added, and the solids were mixed by agitation. The mixture was heated at ca. 140 °C under an atmosphere of purified dinitrogen for 2–3 h. A melt formed at this temperature and turned dark purple. Excess Hmhp was removed by sublimation in vacuo at 160 °C, and the dark purple solid that remained was dissolved in dry toluene. The blue-purple solution was filtered, and then the solvent was removed by evaporation under a reduced pressure, leaving a dark blue solid. This solid was recrystallized from dry CH_2Cl_2/toluene and dried in vacuo (yield 0.34 g, 70%). Anal. Calcd for $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$, $C_{84}H_{96}N_{12}O_{30}Co_{12}$: C, 41.0; H, 3.9; N, 6.8; Co, 28.7. Calcd for $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}\cdot$toluene, $C_{91}H_{104}N_{12}O_{30}Co_{12}$: C, 42.8; H, 4.1; N, 6.6; Co, 27.7. Found: C, 42.2; H, 4.2; N, 6.6; Co, 27.2.

$Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$ is fairly sensitive to moisture, resulting ultimately in the formation of Hmhp and an insoluble light blue material.

Spectroscopic Studies. Mass spectra were recorded on an AEI MS30 instrument; typically, the sample was introduced directly into the ion chamber on the end of the probe, the chamber evacuated, a temperature of 150–250 °C applied, and fragmentation and/or ionization produced by a 70-eV electron beam. Electronic spectra were obtained with a Perkin-Elmer 402 instrument and infrared spectra on a Perkin-Elmer 257 grating spectrometer. Room-temperature magnetic moments were estimated by the NMR method of Evans[9] on a Bruker WP80 spectrometer operating at 80 Hz; each compound was dissolved in $CDCl_3$, and the difference in the ^1H resonance of the small amount of $CHCl_3$ present in the $CDCl_3$, between the solution

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(outer tube) and $CDCl_3$ without solute (inner tube), was recorded.

X-ray Crystallography. Crystals of $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}\cdot x$(toluene) suitable for crystallographic investigation were obtained by slow evaporation of the solvent from a CH_2Cl_2/toluene solution. They were pale purple hexagonal plates of varying thickness with uniaxial optical properties, the unique axis being perpendicular to the major faces. The crystals quickly became crazed and crumbled to a powder when withdrawn from the mother liquor, an indication of loosely held solvent molecules in the structure. Nevertheless, it was possible to cut a piece (dimensions ca. 0.4 mm) from a large plate and seal it in a Lindemann glass capillary. Measurements were made at room temperature on a Stoe-Siemens AED diffractometer, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å).[10]

The space group is $P\bar{3}$, with $a = 24.252$ (3) Å, $c = 16.859$ (3) Å (refined from 2θ values of 30 reflections with $20 < 2\theta < 25°$), $V = 8587.3$ Å^3, and $Z = 2$. Intensities were measured for $7 < 2\theta < 45°$ in a θ/ω scan mode, by a real-time profile-fitting procedure.[11] Rapid falloff of reflection intensity at higher 2θ values suggested high thermal motion and/or disorder. A total of 4081 unique reflections with $F > 3\sigma(F)$ were used for structure determination. Absorption corrections were not applied ($\mu = 11.7$ cm^{-1}).

The main difficulties in the structure determination were the recognition of the unexpected and complex structure and the treatment of solvent disorder. Application of multisolution tangent refinement with random values for all starting phases[12] yielded coordinates for six independent large peaks in a subsequent E map. These were refined as Co, and the C, N, and O atoms were revealed in a series of difference syntheses. Refinement was by a blocked-cascade least-squares method, to a minimum value of $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F) + gF^2$; g was automatically optimized, the final value being 0.0035). Scattering factors were taken from ref 13; no attempt was made to locate or include H atoms. All other atoms of the molecule were assigned anisotropic thermal parameters. R converged to 0.100 and R_g to 0.148 ($R = \sum|\Delta|/\sum|F_o|$; $R_g = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$).

At this stage a difference synthesis showed many peaks of size 0.5–1.0 e Å^{-3} in the considerable spaces between molecules; these were interpreted as disordered solvent, and attempts were made to fit a simple model to some of them. Two hexagonal groups of peaks were identified as possible toluene rings and refined as rigid regular hexagons (C–C = 1.395 Å), with an overall isotropic thermal parameter for each group. R and R_g were reduced to 0.093 and 0.123, respectively. The high thermal parameters ($U = 0.63$ (2) and 0.74 (3) Å^2) demonstrate that the toluene positions are probably only partially occupied. Complete occupancy would give the ideal formula $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}\cdot 6C_7H_8$. No attempt was made to deal with the toluene methyl groups, which are presumably also disordered around the rings.

The rms deviation of a reflection on an absolute scale of $|F_c|$ ($=(\sum w\Delta^2/\sum w)^{1/2}$) was 7.11 electrons and showed no systematic variation with index parity groups or with $\sin\theta$ above ca. 0.15. The higher value of 13.60 electrons for reflections with $\sin\theta < 0.15$ is a direct consequence of the inadequately modeled solvent disorder. The slope of the central, linear portion of a normal probability plot[14] was 1.16; the extreme points showed deviations greater than those required for a linear relationship, as expected in this case.

Observed and calculated structure factors and anisotropic thermal parameters are available as supplementary material. Structural results are given in the following tables: atomic coordinates in Table I and bond lengths and angles and other important intramolecular distances in Table II.

Table I. Atomic Coordinates ($\times 10^4$)[a]

atom	x	y	z
Co(1)	6667	3333	5329 (2)
Co(2)	6667	3333	2766 (2)
Co(3)	6667	3333	7906 (2)
Co(4)	5557 (1)	1900 (1)	5328 (1)
Co(5)	6731 (1)	2094 (1)	6322 (1)
Co(6)	5208 (1)	2772 (1)	4333 (1)
O(1)	5824 (5)	3328 (5)	3349 (6)
C(11)	5867 (8)	3727 (8)	2792 (11)
C(12)	5435 (10)	3945 (9)	2709 (10)
C(13)	5573 (11)	4394 (12)	2039 (11)
C(14)	6088 (11)	4568 (11)	1554 (12)
C(15)	6474 (10)	4337 (9)	1676 (10)
C(16)	7094 (10)	4544 (10)	1225 (12)
N(1)	6369 (6)	3934 (6)	2274 (7)
O(2)	7076 (5)	2779 (5)	7307 (6)
C(21)	7516 (7)	2987 (7)	7860 (9)
C(22)	8005 (9)	2822 (10)	7925 (13)
C(23)	8434 (10)	3114 (11)	8576 (12)
C(24)	8436 (11)	3559 (10)	9065 (12)
C(25)	7945 (9)	3689 (9)	8937 (11)
C(26)	7860 (11)	4161 (12)	9458 (13)
N(2)	7485 (6)	3393 (6)	8367 (7)
O(3)	6367 (4)	1755 (4)	5079 (6)
C(31)	6409 (7)	1285 (6)	4767 (9)
C(32)	5938 (9)	643 (8)	4952 (11)
C(33)	6022 (8)	173 (10)	4598 (12)
C(34)	6543 (9)	341 (8)	4133 (13)
C(35)	6995 (9)	1027 (10)	3989 (13)
C(36)	7636 (12)	1284 (11)	3494 (17)
N(3)	6905 (6)	1470 (6)	4335 (8)
O(4)	5001 (4)	2369 (4)	5577 (6)
C(41)	4441 (8)	2162 (8)	5869 (9)
C(42)	3922 (9)	1556 (10)	5722 (13)
C(43)	3344 (10)	1445 (11)	6110 (17)
C(44)	3297 (10)	1889 (11)	6600 (16)
C(45)	3836 (8)	2466 (10)	6723 (13)
C(46)	3838 (10)	2961 (11)	7203 (13)
N(4)	4392 (6)	2578 (6)	6334 (8)
O(51)	5158 (5)	1212 (5)	6183 (7)
O(52)	6023 (5)	1355 (5)	6900 (7)
C(51)	5428 (9)	1080 (8)	6748 (11)
C(52)	4953 (10)	488 (9)	7257 (12)
O(61)	4946 (5)	1290 (5)	4505 (7)
O(62)	4706 (5)	1906 (6)	3775 (6)
C(61)	4673 (9)	1377 (8)	3963 (14)
C(62)	4246 (10)	834 (9)	3409 (13)
O(7)	6261 (4)	2546 (4)	6087 (6)
O(8)	5952 (4)	2669 (4)	4568 (5)
T(1)	4505 (96)	4149 (32)	−520 (124)
T(2)	4313	3949	259
T(3)	3667	3622	454
T(4)	3211	3494	−130
T(5)	3400	3693	−909
T(6)	4046	4020	−1103
T(7)	1778 (169)	−279 (101)	5008 (29)
T(8)	2324	196	4637
T(9)	2273	468	3932
T(10)	1676	265	3598
T(11)	1129	−209	3969
T(12)	1181	−482	4674

[a] Estimated standard deviations in the last places of figures are given in parentheses.

Results and Discussion

In this initial examination of the complexes of cobalt(II) with mhp, we have investigated the reactions of cobalt(II) acetate with mhp, derived from Na(mhp) or Hmhp. Use of the latter as a reactant and solvent for the substitution of acetate (or other ligands) is potentially attractive, since pure Hmhp melts at 158–160 °C and solutions can be formed at lower temperatures, with acetic acid subsequently removed in vacuo, prior to sublimation of the excess of Hmhp, which occurs reasonably rapidly at 10^{-3} torr and 160 °C. However, in the case of the reaction between cobalt(II) acetate and Hmhp reported here, only partial substitution was achieved. In contrast, in the reaction between Na(mhp) and cobalt(II) acetate, at room temperature, with $CHCl_3$ as a convenient

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Table II

Bond Lengths (Å)[a]			
Co(1)-O(7)	2.090 (9)	Co(1)-O(8)	2.110 (8)
Co(2)-O(1)	2.262 (13)	Co(2)-N(1)	2.094 (17)
Co(3)-O(2)	2.269 (14)	Co(3)-N(2)	2.069 (15)
Co(4)-O(3)	2.201 (13)	Co(4)-O(4)	2.197 (14)
Co(4)-O(51)	2.043 (10)	Co(4)-O(61)	2.030 (11)
Co(4)-O(7)	2.081 (8)	Co(4)-O(8)	2.063 (9)
Co(5)-O(2)	2.197 (10)	Co(5)-O(3)	2.263 (10)
Co(5)-O(52)	2.009 (10)	Co(5)-O(7)	1.975 (13)
Co(5)-O(4a)	2.279 (9)	Co(5)-N(4a)	2.101 (17)
Co(6)-O(1)	2.188 (10)	Co(6)-O(4)	2.262 (10)
Co(6)-O(62)	2.056 (11)	Co(6)-O(8)	1.982 (12)
Co(6)-O(3b)	2.282 (8)	Co(6)-N(3b)	2.064 (4)
Bond Angles (deg)			
O(7)-Co(1)-O(8)	81.0 (3)	O(7)-Co(1)-O(7a)	86.5 (3)
O(7)-Co(1)-O(8a)	110.0 (4)	O(8)-Co(1)-O(8a)	86.9 (3)
O(7)-Co(1)-O(8b)	158.4 (4)	O(1)-Co(2)-N(1)	63.3 (5)
O(1)-Co(2)-O(1a)	102.5 (3)	O(1)-Co(2)-N(1a)	90.6 (5)
N(1)-Co(2)-N(1a)	105.4 (4)	O(1)-Co(2)-N(1b)	162.8 (4)
O(2)-Co(3)-N(2)	61.3 (5)	O(2)-Co(3)-O(2a)	101.7 (3)
O(2)-Co(3)-N(2a)	160.1 (4)	N(2)-Co(3)-N(2a)	106.8 (4)
O(2)-Co(3)-N(2b)	92.3 (3)	O(3)-Co(4)-O(4)	161.2 (3)
O(3)-Co(4)-O(51)	95.8 (5)	O(4)-Co(4)-O(51)	97.2 (5)
O(3)-Co(4)-O(61)	98.0 (5)	O(4)-Co(4)-O(61)	95.4 (5)
O(51)-Co(4)-O(61)	90.7 (4)	O(3)-Co(4)-O(7)	77.1 (4)
O(4)-Co(4)-O(7)	88.7 (4)	O(51)-Co(4)-O(7)	93.3 (4)
O(61)-Co(4)-O(7)	173.9 (5)	O(3)-Co(4)-O(8)	88.8 (4)
O(4)-Co(4)-O(8)	77.1 (4)	O(51)-Co(4)-O(8)	172.7 (5)
O(61)-Co(4)-O(8)	94.2 (4)	O(7)-Co(4)-O(8)	82.3 (3)
O(2)-Co(5)-O(3)	155.1 (5)	O(2)-Co(5)-O(52)	98.1 (4)
O(3)-Co(5)-O(52)	97.0 (4)	O(2)-Co(5)-O(7)	80.8 (5)
O(3)-Co(5)-O(7)	77.8 (4)	O(52)-Co(5)-O(7)	96.9 (5)
O(2)-Co(5)-O(4a)	95.2 (3)	O(3)-Co(5)-O(4a)	77.6 (3)
O(52)-Co(5)-O(4a)	157.6 (5)	O(7)-Co(5)-O(4a)	103.0 (4)
O(2)-Co(5)-N(4a)	99.9 (5)	O(3)-Co(5)-N(4a)	96.9 (5)
O(52)-Co(5)-N(4a)	99.8 (5)	O(7)-Co(5)-N(4a)	163.0 (4)
O(4a)-Co(5)-N(4a)	60.0 (5)	O(1)-Co(6)-O(4)	154.8 (4)
O(1)-Co(6)-O(62)	99.0 (4)	O(4)-Co(6)-O(62)	95.3 (4)
O(1)-Co(6)-O(8)	81.1 (4)	O(4)-Co(6)-O(8)	77.2 (4)
O(62)-Co(6)-O(8)	94.2 (5)	O(1)-Co(6)-O(3b)	95.4 (4)
O(4)-Co(6)-O(3b)	77.5 (4)	O(62)-Co(6)-O(3b)	158.7 (4)
O(8)-Co(6)-O(3b)	103.5 (3)	O(1)-Co(6)-N(3b)	100.4 (6)
O(4)-Co(6)-N(3b)	96.7 (5)	O(62)-Co(6)-N(3b)	102.4 (6)
O(8)-Co(6)-N(3b)	162.8 (5)	O(3b)-Co(6)-N(3b)	59.3 (4)
Selected Intramolecular Distances (Å)			
Co(1)···Co(2)	4.32 (2)	Co(1)···Co(3)	4.35 (2)
Co(1)···Co(4)	3.16 (2)	Co(1)···Co(5)	3.51 (2)
Co(1)···Co(6)	3.52 (2)	Co(2)···Co(6)	4.07 (2)
Co(3)···Co(5)	4.08 (2)	Co(4)···Co(5)	3.13 (2)
Co(4)···Co(5b)	3.95 (2)	Co(4)···Co(6)	3.13 (2)
Co(4)···Co(6a)	3.96 (2)	Co(5)···Co(6a)	3.52 (2)
Co(5)···Co(5a)	5.34 (3)	Co(6)···Co(6a)	5.36 (3)
O(1)···O(8b)	2.86 (4)	O(2)···O(7a)	2.85 (4)

[a] Symmetry operators: (a) $1 - y, x - y, z$; (b) $1 - x + y, 1 - x, z$.

solvent for the reaction product, complete substitution was achieved.

$Co(mhp)_2$, in solution and in the gas phase, appears to be composed of simple monomeric molecules, on the basis of the mass spectrum and of the magnetic moment obtained for $CHCl_3$ solutions of the compound at 305 K. The latter, at 4.8 μ_B, is in the range normally observed for simple high-spin tetrahedral Co(II) complexes,[15] and the former, obtained by heating the material to 170 °C, contained as the highest m/e feature an intense peak at 275, corresponding to $Co(mhp)_2^+$; a weaker peak at $m/e = 167$, corresponding to $Co(mhp)^+$, was also present. No peaks were observed at higher m/e. These observations are in marked contrast to the formation of the diamagnetic dimeric $[Cr(mhp)_2]_2$,[2] which exhibits a strong parent ion peak and other Cr_2 fragments in the mass spectrum. The visible absorption spectrum for $Co(mhp)_2$ in $CHCl_3$ solution consists of a broad absorption maximum centered at 574 nm ($\epsilon = 241$ L mol^{-1} cm^{-1}). The infrared spectrum of the material mulled in Nujol exhibits vibrational frequencies of the mhp group; the most distinctive absorptions occur at 1655, 1610, and 1558 cm^{-1} and are assigned to the ligand $\mathrm{C}\underset{\cdots}{-}\mathrm{N}$, $\mathrm{C}\underset{\cdots}{-}\mathrm{O}$, and $\mathrm{C}\underset{\cdots}{-}\mathrm{C}$ (coupled) stretching modes. A similar profile is observed for the infrared spectrum of the bidentate/bridging mhp ligands in $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$ (vide infra). This behavior contrasts, however, with that observed for *trans*-$Ru(mhp)_2(PPh_3)_2$,[8] which has two bidentate mhp groups[16] and exhibits one strong infrared absorption at 1610 cm^{-1}, a feature also observed for $Co(mhp)_2(bpy)$. Therefore, it is tentatively suggested that, in the solid state, $Co(mhp)_2$ may involve the bidentate mhp ligands bridging to neighboring Co(II) centers as in $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$. Nevertheless, it is suggested that any such bridges are weak and, in contrast to the case for Cr(II), this 3d metal $M(mhp)_2$ complex is a simple monomer in the gas phase and in solution.

Some difficulties were experienced in handling $Co(mhp)_2$, in particular because of its sensitivity to hydrolysis. Further characterization of this compound was sought through the preparation of a derivative that might be more stable in this respect. Thus the synthesis of $Co(mhp)_2(bpy)$ was attempted. This compound is, indeed, much more stable to hydrolysis, presumably because of the blocking of the coordination sites available for initial attack by H_2O on $Co(mhp)_2$. The mass spectrum of $Co(mhp)_2(bpy)$, obtained by heating the material to 250 °C, contained as the principal features peaks corresponding to $Co(mhp)_2^+$ ($m/e = 275$) and bpy (158). The magnetic moment, for the compound dissolved in $CHCl_3$ at 304 K, is estimated to be 5.4 μ_B, in reasonable agreement with values typical of simple octahedral Co(II) complexes.[15] The visible absorption spectrum of a $CHCl_3$ solution consists of a broad band centered at ca. 400 nm and having a rather high intensity ($\epsilon = 670$ L mol^{-1} cm^{-1}) for an "octahedral" complex. This intensity is presumably a consequence of the low-symmetry ligand field about the Co(II), with two different chelates, the mhp ligands having a narrow "bite". In this latter respect, we note that the only complex in which mhp has previously been shown to be a simple bidentate ligand is *trans*-$Ru(mhp)_2(PPh_3)_2$,[16] in which the intraligand O···N separation is 2.18 (1) Å (cf. 2.1 Å for NO_3^-[17]) and the O-Ru-N interbond angle is only 61.8 (2)°. Other, and presumably related, consequences of this bidentate coordination are the C–O (1.354 (5) Å) and C–N (1.331 (8) Å) bond lengths within the mhp ligands in *trans*-$Ru(mhp)_2(PPh_3)_2$, indicating that the electronic structure of the ligand corresponds to that of the enol form, in contrast to the situation for $M_2(mhp)_4$ complexes, where the C–N and C–O bond lengths correspond to a roughly equal mixture of the enol and keto forms.[2] As indicated above, both *trans*-$Ru(mhp)_2(PPh_3)_2$ and $Co(mhp)_2(bpy)$, as solids mulled in Nujol, have only one strong infrared absorption in the region between 1700 and 1500 cm^{-1}, at ca. 1610 cm^{-1}. Accordingly, it is suggested that $Co(mhp)_2(bpy)$ contains bidentate mhp groups, which, unlike those in $Co(mhp)_2$, do not participate in intermolecular Co(II)···O interactions in the solid state and which structurally resemble those in *trans*-$Ru(mhp)_2(PPh_3)_2$.

The formation and structrue of $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$ is surprising, to say the least. The partial substitution of acetate by mhp and the presence of OH groups were not expected when the synthetic procedure was initially conceived; the latter are presumed to derive from the (small quantity of)

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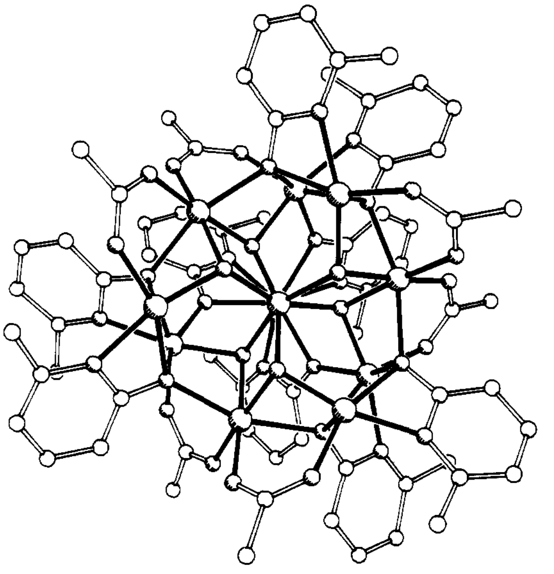

Figure 1. View along the C_3 axis, with bonds to Co filled and other bonds open. The nearer Co(mhp)$_3$ "cap" is omitted from the plot.

water present in the reaction mixture through incomplete drying of the reactants and/or solvents. However, these observations seem minor in comparison to the complexity of the molecular structure of this duodecanuclear cobalt(II) complex.

Structure of $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$. The molecule has exact C_3 and approximate D_3 symmetry (Figure 1) and an approximately spherical shape (closest distances between the centers of molecules measured perpendicular to and within the x–y plane are 8.43 and 7.02 Å, respectively), with mhp and acetate C–H groups at the periphery and an interior network of twelve cobalt atoms linked by bridging hydroxy, acetate, and mhp ligands.

Cobalt Atom Arrangement. Cobalt atoms are of four types. One central (c; Co(1)) and two "axial" (a; Co(2) and Co(3)) atoms lie on the threefold axis. Three others (e; Co(4) and symmetry equivalents) lie in an "equatorial" plane, which is perpendicular to the symmetry axis and contains the central atom. The remaining six atoms (Co(5), Co(6), and symmetry equivalents) lie in two planes 1.68 (1) Å above and below the equatorial plane; by extension of the geographical analogy, we refer to these as "tropical" (t) cobalt atoms. These six Co(t) atoms thus form a trigonal prism, one triangular face of which is rotated by 19.9° with respect to the other. The Co(a) atoms cap the triangular faces, and the Co(e) atoms the prism faces. This Co$_{12}$ arrangement is illustrated in Figure 2, in which one of each type of ligand (vide infra) is also shown; Co⋯Co separations are listed in Table II. Each Co atom forms bonds to six ligand O or N atoms in a distorted-octahedral arrangement. The Co(c) atom has only Co–OH bonds (Figure 1). The Co(a) atoms are each coordinated by three bidentate mhp ligands, through the oxygen atom of which they are linked to Co(t) atoms (Figure 2). Each Co(e) atom forms six Co–O bonds: two to hydroxy groups, two to acetate bridges linking them to Co(t) atoms, and two to mhp ligands, which link them to the same Co(t) atoms (Figure 1). The coordination of the Co(t) atoms is even more complex, each having one bidentate mhp ligand, Co–O bonds to two other mhp ligands, one acetate and one hydroxy ligand (Figure 1). The largest distortions away from ideal octahedral coordination angles (90°) are for the narrow bite of the bidentate mhp ligands (63.3 (5), 61.3 (5), 60.0 (5), and 59.3 (4)°).

Ligands. The hydroxy ligands each bridge three cobalt atoms [Co(c), Co(e), and Co(t)] in a pyramidal arrangement. The acetate groups form bridges between equatorial and tropical cobalt atoms, for which Co(e)⋯Co(t) is 3.13 (2) Å. This Co⋯Co separation is a consequence of the two single-atom bridges that also exist between these pairs of cobalt atoms (one OH and one O of mhp; Co(c) and Co(e), which share two single-atom OH bridges, are separated by 3.16 (2) Å, vide infra), rather than a requirement of the acetate bridge itself. The acetate ligand, acting in this bridging mode, is capable of spanning metal–metal separations covering a wide range, from very short multiple bonds, as in $Mo_2(O_2CCH_3)_4$ (2.093 Å),[18] to long nonbonded separations, as in $[Rh_3O(O_2CCH_3)_6(H_2O)_3]^+$ (3.33 Å).[19]

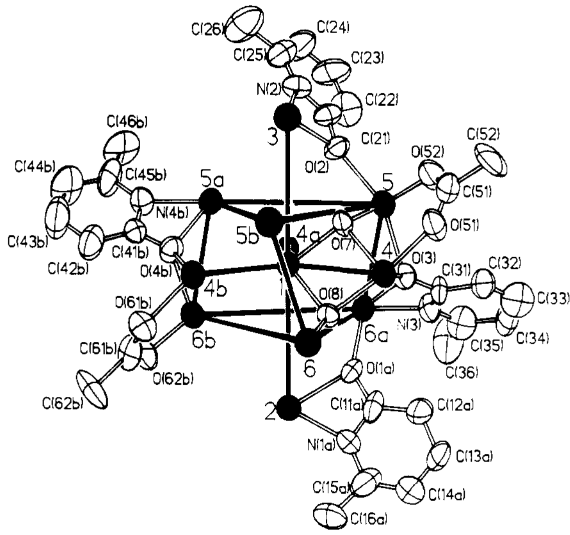

Figure 2. Co$_{12}$ arrangement in $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$ (atoms numbered), together with all the crystallographically independent ligands. Thermal motion is depicted as 50% probability ellipsoids. To minimize overlap, symmetry-equivalent positions of some of the ligands are shown instead of those corresponding to the coordinates in Table I. See Table I for symmetry operator codes.

None of the mhp ligands is of the bridging type found in all $M_2(mhp)_4$ dimers and related complexes. Each mhp ligand is bidentate, forming Co–O and Co–N bonds to the same cobalt atom (axial or tropical). In each case, the oxygen atom is involved in further Co–O bonds, the number of which may be one or two (Figure 2). Coordination of the three-bond oxygen atoms is close to planar, there being a small (0.07 (1) Å) deviation of the oxygen atom from the Co$_3$ plane. For these, and for the four-bond oxygen atoms, the Co–O–C angle within the Co–mhp chelate four-membered ring is less than 90°, and the other angles are correspondingly distorted from ideal trigonal or tetrahedral values, so a simple hybridization model cannot be applied. We note, however, that involvement of the mhp oxygen atoms in one or two additional Co–O bonds is expected to increase the contribution of the enol form to the electronic structure of the ligand. Although the precision of the structural results is limited by the solvent disorder, the mean mhp C–O and C–N bond lengths (1.31 (2) and 1.34 (2) Å) are, indeed, respectively greater and less than those in $M_2(mhp)_4$ dimers[2–5] but not to the extreme degree observed in *trans*-Ru(mhp)$_2$(PPh$_3$)$_2$,[16] where the enol form strongly predominates. A similar behavior has been observed in other complexes in which mhp forms extra bonds with its oxygen atom.[20]

Weak hydrogen bonds appear to exist between the hydroxy groups and the mhp ligands which chelate the axial cobalt atoms. Apart from separations across Co$_2$O$_2$ rings, the shortest

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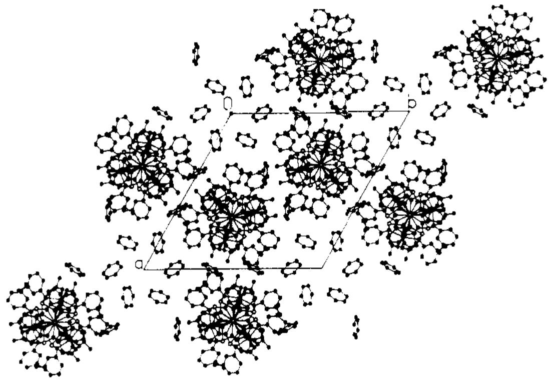

Figure 3. Crystal packing, in parallel projection along the *c* axis.

O⋯O distances (2.85 (4) Å; see Table II) are between hydroxy and mhp three-bond oxygen atoms. The O⋯O vectors are inclined at ca. 17.5° to the Co_2C coordination plane of the mhp oxygen atoms concerned, and at ca. 9.5° to the plane of the three Co atoms that are bridged by the hydroxy ligand, so that the mutual orientations of the two groups are suitable for hydrogen bonding. The deviations of the mhp oxygen atoms from these Co_2O planes (vide supra), although small, are in each case toward the nearby hydroxy ligand. Hydrogen bonding between μ_3-OH and mhp ligands has also been observed in $[Cr_4(mhp)_8(OH)_4]$.[6]

Finally, in this description of the complex molecular structure, we note that the separations between pairs of cobalt atoms reflect the number and nature of the bridges connecting them (see Table II). Thus, the closest Co⋯Co pairs (3.13–3.16 Å) are each linked by two single-atom bridges (2 × OH for Co(c)⋯Co(e) or OH and mhp together with a three-atom acetate bridge for Co(e)⋯Co(t)). A single OH bridge spans Co(c)⋯Co(t) separations of 3.51–3.52 Å. The mhp oxygen atoms appear not to require such small separations: two such bridges span the 3.52-Å Co(t)⋯Co(t) separation, and a single bridge spans those of 3.95–4.08 Å for Co(a)⋯Co(t) and Co(t)⋯Co(t). Pairs of cobalt atoms not directly linked by ligands are separated by >4.3 Å.

Solvent. It is clear that the crystal structure contains disordered solvent molecules, which appear to be toluene rather than CH_2Cl_2. The positions of the toluene molecules located in the structure determination can be seen in Figure 3. The two symmetry-related $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$ molecules in the unit cell have almost the same height (Co(1) at z = 0.5329 (2) and 0.4671 (2) Å, a difference of 1.1 Å). Between the molecules there are channels running parallel to the *c* axis, and the solvent molecules lie in these channels. All distances between the toluene ring atoms and atoms of the complex molecule, and between different toluene molecules, are >3.6 Å. This explains the easy loss of solvent when crystals are removed from the mother liquor. The number of toluene molecules per complex molecule, even if no solvent is lost from the crystal, is unknown. The sample used for chemical analysis would also be subject to solvent loss, and as noted above, best agreement is obtained for approximately a 1:1 ratio. In view of the large size of the cavities, the presence of some CH_2Cl_2 in freshly prepared crystals still in contact with mother liquor cannot be ruled out; as reported above, however, both X-ray crystallography and chemical analysis failed to indicate any. Crystallization from other solvents was not attempted.

Spectra. The mass spectrum of $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$, obtained for the compound sublimed at 250 °C, reflects some of the complexity of the molecular structure. In contrast with the mass spectra of $Co(mhp)_2$ and $Co(mhp)_2(bpy)$, a series of intense peaks is observed between *m*/*e* values of 802 and 334 (with a large number of others below the latter value). The precise assignment is hampered, because mass number 59 corresponds to both Co and CH_3CO_2 and because there is no isotropic profile for cobalt. The interpretation of the principal features is included in the supplementary material.

The magnetic moment of $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$, dissolved in $CHCl_3$ at 304 K, corresponds to an average of ca. 3.0 μ_B/Co atom. This is significantly lower than the values obtained for $Co(mhp)_2$ and $Co(mhp)_2(bpy)$ and suggests the presence of intramolecular magnetic exchange between the metal centers, probably via the bridging ligands rather than by direct Co⋯Co interactions. The visible absorption spectrum, for the compound dissolved in $CHCl_3$, shows a broad absorption centered at ca. 580 nm (ϵ = 396 L mol^{-1} cm^{-1}). The infrared spectrum (Nujol mull) shows evidence for OH groups, with a broad band centered at 3450 cm^{-1}, suggesting hydrogen bonding.[21] Bands at ca. 1675 and 1460 cm^{-1} are assigned as the symmetric and antisymmetric CO_2 stretching frequencies of the μ-acetate groups.[21] In the region between 1500 and 1700 cm^{-1}, three other absorptions are seen at ca. 1555, 1610, and 1655 cm^{-1} (the last forms a shoulder on the 1675-cm^{-1} peak). As discussed for $Co(mhp)_2$ above, these are considered to represent the $C\overset{..}{-}N$, $C\overset{..}{-}O$, and $C\overset{..}{-}C$ (coupled) stretching modes of the bidentate/bridging mhp ligands.

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Registry No. $Co(mhp)_2$, 85166-51-4; $Co(mhp)_2(bpy)$, 85220-63-9; $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}$, 85234-82-8; $Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}\cdot x$(toluene), 85234-83-9.

Supplementary Material Available: Listings of bond lengths and angles within the ligands, mass spectrum interpretations, anisotropic thermal parameters, and observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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