Table V. Crystal Data and Data Collection Solution, and Refinement Parameters for $Ir_2(SO_2)_2(CO)_2Cl_2(\mu\text{-dpma})_2\cdot 3CHCl_3\cdot 0.5CH_2Cl_2$ (**5**) and $[Ir_2Au(SO_2)(CO)_2Cl_2(\mu\text{-dpma})_2][HSO_4]\cdot 0.32SO_2\cdot 1.23H_2O$ (**6**)

	5	**6**
formula	$C_{68}H_{60}As_2Cl_2$-$Ir_2O_6P_4S_2$	$C_{66}H_{61.5}AuAs_2Cl_2$-$Ir_2O_{9.9}P_4S_{2.3}$
fw	2120.9	2012.92
color and habit	yellow green needles	red prisms
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P1$
a, Å	14.699 (4)	12.548 (4)
b, Å	15.351 (6)	15.721 (4)
c, Å	38.026 (10)	20.556 (5)
α, deg		76.97 (2)
β, deg	100.03 (3)	73.60 (2)
γ, deg		83.35 (2)
V, Å^3	8449 (5)	3784 (2)
T, K	130	130
Z	4	2
d_{calcd}, g cm^{-3} (130 K)	1.67	1.77
radiation Å	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα), cm^{-1}	46.6	67.7
range of transmissn factors	0.51–0.63	0.27–0.48
cryst dimens, mm	0.12 × 0.13 × 0.27	0.13 × 0.20 × 0.37
R^a	0.078	0.059
$R_w{}^a$ [$w = 1/(\sigma^2(F_o)$]	0.079	0.065

[a] $R = \sum||F_o| - |F_c||/|F_o|$, and $R_w = \sum||F_o| - |F_c||\ w^{1/2}/\sum|F_o w^{1/2}|$.

smaller crystals were used to collect the infrared data. However, the yield of crystals was low. Crystal data and data collection parameters are given in Table V and in the supplementary material. Data analysis and refinement follow the procedure outlined above. Two low-angle reflections that were affected by extinction were removed from the data. One site in the structure is shared by a molecule of water and a molecule of SO_2. Two models were devised and compared. A group occupancy for the SO_2 molecule refined to 0.313 (9). The thermal parameter of the oxygen of the water molecule (O(10)) at the center of symmetry was fixed at 0.07 Å^2 and the occupancy allowed to refine. It converged at 0.23 (2). In the alternative model to eliminate a suspicious S···S contact at 3.25 Å, the water oxygen occupancy was reset to 0.5 minus the group occupancy of the SO_2 group and refined; the thermal parameters were kept free. This yielded an occupancy of 0.34 (1) for the SO_2 and 0.16 (1) for the water. The water oxygen thermal parameter in this case refined to 0.03 (1) Å^2 while the SO_2 thermal parameters were essentially unchanged. The two models appear satisfactorily similar. The data reported come from the first model. In the last cycles of refinement all non-hydrogen atoms except the disordered SO_2 and water oxygen were assigned anisotropic thermal parameters. In the final difference map the largest feature was 3.1 e Å^{-3} in height, 0.94 Å from Au. Several remaining peaks were also large, but were in the vicinity of heavy atoms and not of any chemical significance.

There are two O···O distances that are indicative of hydrogen bonding, O(4)···O(9)/3.02 (1) Å, and O(6)···O(12) = 2.68 (7) Å. The first corresponds to one of the oxygens of the terminally bound SO_2 and a molecule of H_2O; the second corresponds to one of the $HSO_4{}^-$ oxygens and one of the partially occupied SO_2 oxygens. However, definitive crystallographic identification of the anion as bisulfate (rather than sulfate) was not possible.

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Supplementary Material Available: Tables of crystal data and structural determination parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for **4** and **5** (15 pages); listings of observed and calculated structure factors (85 pages). Ordering information is given on any current masthead page.

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Aluminum and Gallium Complexes of 1-Ethyl-3-hydroxy-2-methyl-4-pyridinone: A New Exoclathrate Matrix

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1-Ethyl-3-hydroxy-2-methyl-4-pyridinone and its aluminum(III) and gallium(III) complexes have been prepared and characterized; all three compounds have been studied by single-crystal X-ray diffraction. The uncomplexed ligand $C_8H_{11}NO_2$ (HL) crystallized in the orthorhombic space group *Pbca* with following the crystal parameters: a = 12.5907 (8) Å,b = 11.7477 (6) Å, c = 11.0040 (6) Å,Z = 8. The complexes $M(C_8H_{10}NO_2)_3\cdot 12H_2O$ ($ML_3\cdot 12H_2O$) are isostructural for M = Al and Ga, crystallizing in the trigonal space group $P\bar{3}$ with following the crystal parameters for Al (Ga): a = 17.1734 (8) Å, (17.247 (1) Å), c = 6.827 (1) Å (6.830 (2) Å), Z = 2. For the three compounds HL, $AlL_3\cdot 12H_2O$, and $GaL_3\cdot 12H_2O$, respectively, the data were refined by using 1228, 1157, and 1918 reflections with $I \geq 3[\sigma(I)]$ to R values of 0.053, 0.032, and 0.029 and R_w values of 0.085, 0.038, and 0.036. The two metal complexes form rigidly *fac* geometries with extensive hydrogen bonding to channels of water molecules involving every available oxygen atom in the unit cell. This structure is an exoclathrate. The Al and Ga complexes show "tucked away" ethyl units that allow the structural integrity of the exoclathrate lattice (including the water channels) to be maintained. On comparison of six exoclathrate crystal structures, a trend was noticed toward deformation of the metal complex rather than the hexagonal channels of water molecules in order to accommodate changes in metal ion or N substituent.

The recent discovery of the exoclathrate lattice, which incorporates hexagonal channels of water molecules hydrogen bonded to tris(3-hydroxy-1,2-dimethyl-4-pyridinonato)metal(III) units (metal = Al[1,2] Ga,[2] In,[3] Fe[4]), has prompted a search for other examples of this complex binding array. Through variation of the substituent on the ring nitrogen atom, this search is being undertaken in metal/ligand systems that are closely related to those in which the lattice was first discovered.

In an effort to study the limitations of the exoclathrate lattice, we have replaced the *N*-methyl group of the ligand with an *N*-ethyl substituent; we report here the Al and Ga complexes of 1-

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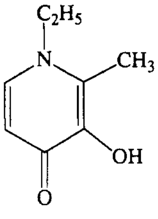
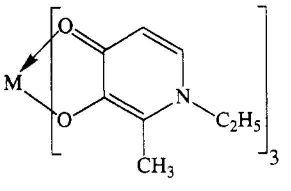
ethyl-3-hydroxy-2-methyl-4-pyridinone (HL) including the crystal structures of the uncomplexed ligand and the complexes ($ML_3 \cdot 12H_2O$, M = Al, Ga). The family of N-substituted 3-hydroxy-4-pyridinones is of considerable interest because it forms very stable complexes with the ions Al^{3+},[5] Ga^{3+},[6] In^{3+},[6] and Fe^{3+}.[7] This stability has led to the study of the ligands as possible chelators of Al,[8] Ga,[6] and Fe[9] in vivo.



HL



ML_3, M = Al, Ga

Experimental Section

The procedures followed and reagents used were similar to those previously detailed.[2,3,10] Lower yield and/or more difficult preparations of 1-ethyl-3-hydroxy-2-methyl-4-pyridinone have been reported.[11,12]

1-Ethyl-3-hydroxy-2-methyl-4-pyridinone, HL. A solution of maltol (3-hydroxy-2-methyl-4-pyrone, 2.52 g, 20.0 mmol), 70% ethylamine in water (13.3 g, 206 mmol), and 40 mL of water was cooled in an ice bath. HCl (6 N, 30 mL) was slowly added and the pH adjusted to 9.8. The reaction mixture was heated for 24 h and then transferred to a continuous liquid–liquid extractor; the product was extracted into 100 mL of CH_2Cl_2 for 6 h. Evaporation of the solvent left a brown solid that was washed with cold acetone. Sublimation gave 1.80 g (58% yield) of a white powder, mp 205 °C dec. Anal. Calcd (found) for $C_8H_{11}NO_2$: C, 62.72 (62.56); H, 7.25 (7.28); N, 9.14 (8.98). ^1H NMR spectrum (δ at 400 MHz in D_2O, atom numbering as for crystallographic results): 1.26 (t, 3 H, $C(8)H_3$), 2.33 (s, 3 H, $C(1)H_3$), 4.00 (q, 2 H, $C(7)H_2$), 6.43 (d, 1 H, C(5)H), 7.56 (d, 1 H, C(6)H). IR spectrum (cm^{-1}, KBr disk): 3180 (ν_{OH}); 1630, 1575, 1530, 1510 ($\nu_{C=O}$ and ν_{ring}). Electron-impact mass spectrum (*m/e*): 153 (M^+), 125, 124, 97, 96. Electronic spectrum (H_2O): λ_{max} = 279 nm (ϵ = 14 200 L mol^{-1} cm^{-1}). Solubility in water (25 °C): 570 mM. 1-Octanol/water partition coefficient (*p*) = 0.43.

Tris(1-ethyl-3-hydroxy-2-methyl-4-pyridinonato)aluminum(III), AlL_3. HL (422 mg, 2.89 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (360 mg, 0.96 mmol) were dissolved in 25 mL of water; a pale pink solution of pH 2.2 resulted. The pH was raised to 7 via the slow addition of 2 N NaOH, and the solution was then heated to 70 °C for 30 min. The cloudy yellow reaction mixture was then transferred to a continuous liquid–liquid extractor and the product extracted into CH_2Cl_2 (75 mL) over 12 h. The organic layer was removed under reduced pressure. The resulting pale pink solid was washed with diethyl ether and dried at 80 °C overnight in vacuo to give 425 mg (92% yield) of complex, mp 250 °C dec. Anal. Calcd (found) for $C_{24}H_{30}AlN_3O_6$: C, 59.61 (59.72); H, 6.27 (6.25); N, 8.69 (8.90). ^1H NMR spectrum (δ at 400 MHz in D_2O): 1.30 (t, 3 H, $C(8)H_3$), 2.32 (s, 3 H, $C(1)H_3$), 4.08 (q, 2 H, $C(7)H_2$), 6.48 (d, 1 H, C(5)H), 7.53 (d, 1 H, C(6)H). IR spectrum (cm^{-1}, KBr disk): 1600, 1555, 1515, 1490 ($\nu_{C=O}$ and ν_{ring}); 705, 580, 460 (ν_{Al-O}). Fast-atom-bombardment mass spectrum (FABMS) (*m/e*): 484 (HML_3^+), 331 (ML_2^+). Electronic spectrum (H_2O): λ_{max} = 292 nm (ϵ = 30 700 L mol^{-1} cm^{-1}). Solubility in water (25 °C): 19 mM. *p* = 0.021. ^{27}Al NMR (H_2O): 37 ppm ($W_{1/2}$ = 780 Hz).

Tris(1-ethyl-3-hydroxy-2-methyl-4-pyridinonato)gallium(III) Hydrate, $GaL_3 \cdot H_2O$. A procedure similar to that for AlL_3 using HL (669 mg, 4.37 mmol) and 1 mL of 1.45 M aqueous $GaCl_3$ solution dissolved in 15 mL of water yielded 652 mg of an off-white powder (85% yield), mp 240 °C dec. Anal. Calcd (found) for $C_{24}H_{32}GaN_3O_7$: C, 53.85 (53.52); H, 5.85 (6.00); N, 7.85 (7.72). ^1H NMR spectrum (δ at 400 MHz in D_2O): 1.30 (t, 3 H, $C(8)H_3$), 2.36 (s, 3 H, $C(1)H_3$), 4.08 (q, 2 H, $C(7)H_2$), 6.54 (d, 1 H, C(5)H), 7.52 (d, 1 H, C(6)H). IR spectrum (cm^{-1}, KBr disk): 3300 (ν_{OH}); 1600, 1555, 1515, 1490 ($\nu_{C=O}$ and ν_{ring}); 705, 565, 410 (ν_{Ga-O}). FABMS (*m/e*): 526/528 (HML_3^+), 373/375 (ML_2^+). Electronic spectrum (H_2O): λ_{max} = 293 nm (ϵ = 30 800 L mol^{-1} cm^{-1}). Solubility in water (25 °C): 11 mM. *p* = 0.023.

Table I. Crystallographic Data[a] for HL, $AlL_3 \cdot 12H_2O$, and $GaL_3 \cdot 12H_2O$

	HL	$AlL_3 \cdot 12H_2O$	$GaL_3 \cdot 12H_2O$
formula	$C_8H_{11}NO_2$	$C_{24}H_{54}AlN_3O_{18}$	$C_{24}H_{54}GaN_3O_{18}$
fw	153.2	699.7	742.4
space group	*Pbca*	$P\bar{3}$	$P\bar{3}$
a, Å	12.5907 (8)	17.1734 (8)	17.247 (1)
b, Å	11.7477 (6)		
c, Å	11.0040 (6)	6.827 (1)	6.830 (2)
V, Å^3	1627.6 (3)	1743.7 (3)	1759.4 (1)
Z	8	2	2
ρ_{calcd}, g cm^{-3}	1.25	1.33	1.40
radiation	Cu Kα	Cu Kα	Mo Kα
$\lambda_{K\alpha}$, Å	1.541 78	1.541 78	0.710 69
transm coeff	0.853–1.0	0.928–1.0	0.965–1.0
μ (Cu or Mo Kα), cm^{-1}	7.04	11.56	8.50
T, °C	21	21	21
R	0.053	0.032	0.029
R_w	0.085	0.038	0.036

[a] Rigaku AFC6S diffractometer; calculations performed on a VAX-based TEXRAY system (Molecular Structure Corp.); $R = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/\sigma^2(F)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (0.035F_o^2)^2](Lp)^2$ where *S* = scan rate, *C* = peak count, *R* = scan time/background time, *B* = background count, *Lp* = Lorentz–polarization factor, and the function minimized was $\sum w(|F_o| - |F_c|)^2$.

Crystallographic Analyses. Abbreviated crystallographic data for HL, $AlL_3 \cdot 12H_2O$, and $GaL_3 \cdot 12H_2O$ appear in Table I (complete details are in Table SIX in the supplementary material). Final unit cell parameters were obtained from least-squares refinement by using the setting angles of 25 reflections with 2θ = 93–115° for HL, 60–80° for $AlL_3 \cdot 12H_2O$, and 22–33° for $GaL_3 \cdot 12H_2O$. The intensities of three standard reflections, measured each 150 reflections, were essentially constant throughout the data collections. Data for all three compounds were corrected for absorption (analytical method).

The structure of HL was solved by direct methods, and the structures of $ML_3 \cdot 12H_2O$ (M = Al, Ga) are isomorphous with those of tris(3-hydroxy-1,2-dimethyl-4-pyridinonato)metal(III) dodecahydrate (metal = Al,[1,2] Ga,[2] In[3]). The non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were refined (isotropic thermal parameters) except H(6) in $AlL_3 \cdot 12H_2O$, which was kept fixed in an observed position. This hydrogen atom refined to an unreasonable position and a peak appeared in the original position on a subsequent difference Fourier synthesis. As found for the previous dodecahydrate structures,[1-3] one of the protons in a $(H_2O)_6$ ring was disordered in $GaL_3 \cdot 12H_2O$.

Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 13. Final coordinates and equivalent isotropic thermal parameters ($B_{eq} = {}^4/_3 \sum_i \sum_j c\vec{a}_i \cdot \vec{a}_j \beta_{ij}$) are given in Table II. Bond lengths, bond angles, and hydrogen-bonding data are given in Tables III–V, respectively. Anisotropic thermal parameters, intramolecular distances and bond angles involving hydrogen atoms, least-squares planes, and torsion angles for the three compounds are included as supplementary material (Tables SI–SV, respectively) as are tables of observed and calculated structure factor amplitudes for each of the compounds (Tables SVI–SVIII).

Results and Discussion

The exoclathrate lattice structure is not limited to metal(III) complexes of 3-hydroxy-1,2-dimethyl-4-pyridinone. Dodecahydrate tris(1-ethyl-3-hydroxy-2-methyl-4-pyridinonato)metal(III) complexes of aluminum and gallium are easily prepared and crystallized from aqueous solution. Crystallography was of central importance in the solid-state study of the hydrogen bonding in these analogues. Of particular interest was the disposition of the bulkier ethyl group and its effect on the lattice.

Most of the gross structural features of the exoclathrate lattice have been well-documented:[2,3] the ice-I_h hexagonal water channels (in the corners of the unit cell), which are comprised of homo-

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Table II. Positional and Equivalent Isotropic Thermal Parameters, B_{eq}, for HL, $AlL_3\cdot 12H_2O$, and $AlL_3\cdot 12H_2O$

atom	x	y	z	B_{eq}, Å^2	atom	x	y	z	B_{eq}, Å^2
				$C_8H_{11}NO_2$					
O(1)	0.6157 (1)	0.0325 (1)	0.1408 (2)	4.43 (8)	H(1B)	0.766 (3)	−0.008 (3)	0.403 (3)	8 (1)
O(2)	0.4477 (1)	−0.1035 (2)	0.0769 (1)	4.41 (8)	H(1A)	0.728 (3)	0.065 (4)	0.307 (4)	9 (1)
N	0.5665 (2)	−0.1174 (2)	0.4200 (2)	4.09 (9)	H(1C)	0.693 (4)	0.078 (4)	0.436 (4)	10 (1)
C(1)	0.7042 (3)	0.0277 (3)	0.3735 (3)	5.2 (1)	H(1)	0.578 (3)	0.036 (3)	0.070 (4)	8 (1)
C(2)	0.6124 (2)	−0.0447 (2)	0.3369 (2)	3.68 (9)	H(5)	0.392 (3)	−0.223 (3)	0.251 (3)	6.2 (7)
C(3)	0.5712 (2)	−0.0403 (2)	0.2218 (2)	3.31 (8)	H(6)	0.463 (2)	−0.235 (3)	0.456 (3)	4.9 (6)
C(4)	0.4831 (2)	−0.1088 (2)	0.1837 (2)	3.52 (9)	H(7B)	0.642 (3)	−0.063 (3)	0.582 (3)	5.9 (7)
C(5)	0.4437 (2)	−0.1827 (3)	0.2739 (2)	4.8 (1)	H(7A)	0.565 (3)	−0.148 (3)	0.616 (3)	6.3 (8)
C(6)	0.4846 (2)	−0.1850 (2)	0.3873 (3)	4.8 (1)	H(8C)	0.755 (3)	−0.198 (3)	0.492 (3)	7.2 (8)
C(7)	0.6099 (3)	−0.1320 (3)	0.5446 (2)	5.0 (1)	H(8B)	0.701 (3)	−0.229 (3)	0.653 (4)	9 (1)
C(8)	0.6920 (3)	−0.2225 (3)	0.5493 (3)	5.8 (2)	H(8A)	0.659 (3)	−0.297 (3)	0.513 (3)	7.2 (8)
				$Al(C_8H_{10}NO_2)_3\cdot 12H_2O$					
Al	$^2/_3$	$^1/_3$	−0.0948 (1)	2.25 (3)	H(2)	0.728 (3)	0.255 (4)	0.48 (1)	5.2 (8)
O(1)	0.61767 (8)	0.22901 (8)	0.0641 (2)	2.76 (4)	H(3)	0.227 (4)	0.101 (3)	0.046 (8)	4.7 (7)
O(2)	0.56187 (8)	0.26308 (8)	−0.2553 (2)	2.74 (4)	H(4)	0.159 (5)	0.112 (5)	−0.03 (1)	6 (1)
O(3)	0.7335 (1)	0.2280 (1)	0.3671 (3)	4.51 (6)	H(5)	0.148 (3)	0.023 (4)	0.516 (7)	4.6 (7)
O(4)	0.1857 (1)	0.0821 (1)	−0.0358 (3)	4.66 (6)	H(6)	0.1933	0.1010	0.6674	5.5
O(5)	0.1838 (1)	0.0749 (1)	0.5503 (3)	4.69 (6)	H(7)	0.374 (4)	0.197 (3)	0.297 (7)	4.9 (7)
O(6)	0.3157 (2)	0.1695 (1)	0.2544 (4)	4.96 (7)	H(8)	0.284 (4)	0.151 (4)	0.34 (1)	5.0 (8)
N	0.4007 (1)	0.02766 (9)	0.0267 (2)	2.99 (5)	H(9)	0.504 (5)	0.017 (6)	0.30 (1)	6 (1)
C(1)	0.5136 (1)	0.0675 (1)	0.2927 (3)	3.66 (7)	H(10)	0.477 (5)	0.057 (4)	0.39 (1)	6 (1)
C(2)	0.4831 (1)	0.0875 (1)	0.1040 (3)	2.75 (5)	H(11)	0.578 (6)	0.087 (5)	0.29 (1)	7 (1)
C(3)	0.5372 (1)	0.1673 (1)	0.0047 (2)	2.52 (5)	H(12)	0.399 (2)	0.131 (2)	−0.355 (6)	3.8 (5)
C(4)	0.5071 (1)	0.1869 (1)	−0.1730 (2)	2.52 (5)	H(13)	0.316 (2)	0.006 (2)	−0.182 (4)	3.1 (5)
C(5)	0.4219 (1)	0.1239 (1)	−0.2432 (3)	3.00 (6)	H(14)	0.375 (3)	−0.080 (3)	0.166 (7)	4.7 (7)
C(6)	0.3709 (1)	0.0453 (1)	−0.1397 (3)	3.23 (6)	H(15)	0.300 (4)	−0.101 (4)	0.013 (8)	5.5 (8)
C(7)	0.3405 (1)	−0.0590 (1)	0.1260 (3)	3.69 (6)	H(16)	0.249 (6)	−0.100 (6)	0.35 (1)	7 (1)
C(8)	0.2894 (2)	−0.0488 (2)	0.2933 (5)	4.73 (9)	H(17)	0.320 (5)	−0.011 (6)	0.37 (1)	6 (1)
H(1)	0.708 (3)	0.241 (3)	0.285 (7)	4.2 (6)	H(18)	0.276 (4)	−0.014 (5)	0.30 (1)	6 (1)
				$Ga(C_8H_{10}NO_2)_3\cdot 12H_2O$					
Ga	$^2/_3$	$^1/_3$	−0.09892 (6)	1.92 (1)	H(3)	0.230 (3)	0.124 (3)	0.038 (7)	10 (1)
O(1)	0.6105 (1)	0.2256 (1)	0.0655 (2)	2.30 (5)	H(4)	0.160 (3)	0.058 (5)	−0.018 (7)	1 (1)
O(2)	0.7012 (1)	0.2593 (1)	−0.2626 (2)	2.36 (5)	H(4a)	0.148 (5)	0.132 (4)	0.012 (9)	5 (1)
O(3)	0.7754 (2)	0.2663 (2)	0.3616 (3)	4.18 (9)	H(5)	0.157 (2)	0.132 (2)	0.523 (5)	6 (1)
O(4)	0.1845 (2)	0.1041 (2)	−0.0373 (3)	4.17 (9)	H(6)	0.194 (2)	0.115 (2)	0.666 (5)	5.4 (9)
O(5)	0.1831 (2)	0.1093 (2)	0.5500 (3)	4.29 (9)	H(7)	0.363 (3)	0.177 (3)	0.292 (6)	7 (1)
O(6)	0.3132 (2)	0.1474 (2)	0.2528 (4)	4.6 (1)	H(8)	0.289 (3)	0.141 (3)	0.351 (6)	7 (1)
N	0.6268 (1)	0.0255 (1)	0.0260 (3)	2.46 (7)	H(9)	0.522 (2)	0.090 (3)	0.303 (5)	7 (1)
C(1)	0.5556 (2)	0.0663 (2)	0.2912 (4)	3.2 (1)	H(10)	0.513 (3)	0.010 (3)	0.306 (6)	9 (1)
C(2)	0.6047 (1)	0.0857 (1)	0.1027 (3)	2.24 (7)	H(11)	0.594 (2)	0.092 (2)	0.396 (5)	7 (1)
C(3)	0.6302 (1)	0.1648 (1)	0.0022 (3)	2.00 (7)	H(12)	0.731 (1)	0.127 (1)	−0.358 (3)	2.3 (5)
C(4)	0.6791 (1)	0.1837 (1)	−0.1759 (3)	2.01 (7)	H(13)	0.689 (2)	−0.001 (2)	−0.188 (4)	3.6 (6)
C(5)	0.7007 (2)	0.1204 (2)	−0.2436 (3)	2.52 (8)	H(14)	0.601 (2)	−0.099 (2)	0.027 (4)	3.9 (6)
C(6)	0.6740 (2)	0.0434 (2)	−0.1418 (3)	2.76 (8)	H(15)	0.539 (2)	−0.086 (2)	0.171 (4)	4.4 (7)
C(7)	0.6003 (2)	−0.0607 (2)	0.1266 (4)	3.3 (1)	H(16)	0.724 (3)	−0.027 (2)	0.234 (5)	7 (1)
C(8)	0.6622 (2)	−0.0505 (2)	0.2913 (5)	4.3 (1)	H(17)	0.663 (2)	−0.010 (2)	0.394 (5)	7 (1)
H(1)	0.770 (2)	0.294 (2)	0.284 (5)	5 (1)	H(18)	0.645 (2)	−0.105 (2)	0.342 (5)	5.8 (8)
H(2)	0.753 (2)	0.270 (2)	0.457 (5)	5.1 (9)					

Table III. Bond Lengths (Å) for HL and the $ML_3\cdot 12H_2O$ Complexes with Estimated Standard Deviations in Parentheses

	HL	M = Al	M = Ga
M–O(1)		1.894 (1)	1.962 (1)
M–O(2)		1.930 (1)	2.000 (1)
O(1)–C(3)	1.357 (3)	1.317 (2)	1.327 (2)
O(2)–C(4)	1.258 (3)	1.297 (2)	1.303 (2)
N–C(6)	1.351 (3)	1.342 (3)	1.349 (3)
N–C(2)	1.378 (3)	1.373 (2)	1.376 (3)
N–C(7)	1.485 (3)	1.485 (2)	1.488 (3)
C(1)–C(2)	1.490 (4)	1.494 (2)	1.485 (3)
C(2)–C(3)	1.370 (3)	1.388 (2)	1.387 (3)
C(3)–C(4)	1.433 (3)	1.424 (2)	1.422 (3)
C(4)–C(5)	1.410 (3)	1.399 (2)	1.396 (3)
C(5)–C(6)	1.350 (4)	1.380 (3)	1.360 (3)
C(7)–C(8)	1.484 (4)	1.504 (3)	1.500 (4)

dromic circles[14] of water molecules; the various O···H hydrogen bond donor types;[15] the use of every hydrogen-bonding donor in the unit cell as such; the hydrogen bonding by water molecules

Table IV. Bond Angles (deg) for HL and the $ML_3\cdot 12H_2O$ Complexes with Estimated Standard Deviations in Parentheses

	HL	M = Al	M = Ga
O(1)–M–O(2)		84.23 (5)	83.03 (6)
O(1)–M–O(1)′		90.46 (6)	90.52 (6)
O(1)–M–O(2)′		94.87 (5)	95.29 (6)
O(2)–M–O(1)′		172.50 (5)	171.34 (5)
O(2)–M–O(2)′		90.93 (6)	91.79 (6)
M–O(1)–C(3)		112.1 (1)	111.2 (1)
M–O(2)–C(4)		111.3 (1)	110.7 (1)
C(2)–N–C(6)	120.5 (2)	121.6 (1)	120.9 (2)
C(2)–N–C(7)	122.0 (2)	121.0 (2)	121.1 (2)
C(6)–N–C(7)	117.3 (2)	117.4 (2)	118.0 (2)
N–C(2)–C(1)	120.0 (2)	120.5 (2)	120.2 (2)
N–C(2)–C(3)	118.6 (2)	118.8 (2)	118.8 (2)
C(1)–C(2)–C(3)	121.5 (2)	120.7 (2)	121.0 (2)
O(1)–C(3)–C(2)	118.3 (2)	124.0 (2)	122.4 (2)
O(1)–C(3)–C(4)	118.8 (2)	115.5 (1)	117.0 (2)
C(2)–C(3)–C(4)	122.9 (2)	120.5 (1)	120.6 (2)
O(2)–C(4)–C(3)	121.3 (2)	116.2 (1)	117.5 (2)
O(2)–C(4)–C(5)	124.3 (2)	125.6 (1)	124.9 (2)
C(3)–C(4)–C(5)	114.3 (2)	118.1 (1)	117.6 (2)
C(4)–C(5)–C(6)	121.9 (2)	119.2 (2)	120.1 (2)
N–C(6)–C(5)	121.8 (2)	121.8 (2)	122.0 (2)
N–C(7)–C(8)	111.8 (2)	112.6 (2)	112.5 (2)

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(14) Saenger, W. *Nature* (*London*) **1979**, *279*, 343; **1979**, *280*, 848.

(15) Falk, M.; Knop, O. In *Water*: *A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, London, 1973; Vol. 2 pp 55–113.

Table V. Hydrogen-Bonding Distances and Angles in the Complexes $ML_3{\cdot}12H_2O$

	O–H, Å		H···O, Å		O···O, Å		O–H···O, deg	
interaction	Al	Ga	Al	Ga	Al	Ga	Al	Ga
O(3)–H(1)···O(1)	0.81 (5)	0.75 (4)	2.10 (5)	2.14 (4)	2.877 (2)	2.883 (3)	161 (4)	172 (4)
O(3)–H(2)···O(2)	0.92 (7)	0.77 (3)	1.95 (7)	2.08 (3)	2.838 (2)	2.843 (3)	163 (5)	168 (3)
O(4)–H(3)···O(6)	0.83 (7)	0.85 (4)	1.99 (7)	1.95 (5)	2.795 (3)	2.784 (3)	166 (4)	167 (4)
O(4)–H(4)···O(4)[a]	0.85 (8)	0.71 (7)	1.97 (8)	2.11 (7)	2.811 (2)	2.810 (3)	170 (6)	172 (5)
O(4)–H(4a)···O(4)[a]		1.0 (1)		1.8 (1)		2.810 (3)		166 (5)
O(5)–H(6)···O(4)	0.89 (1)	0.81 (3)	2.04 (6)	2.03 (4)	2.828 (3)	2.821 (3)	146	164 (3)
O(5)–H(5)···O(5)	0.82 (6)	0.76 (3)	2.02 (6)	2.08 (4)	2.833 (2)	2.835 (3)	171 (4)	175 (4)
O(6)–H(7)···O(3)	0.91 (6)	0.79 (4)	1.86 (6)	2.00 (4)	2.771 (3)	2.763 (3)	173 (4)	165 (4)
O(6)–H(8)···O(5)	0.76 (8)	0.77 (4)	2.11 (8)	2.12 (4)	2.859 (3)	2.849 (4)	168 (5)	159 (4)

[a] For M = Ga, the hydrogen attached to O(4) was disordered and was resolved as 50% H(4) and 50% H(4a).

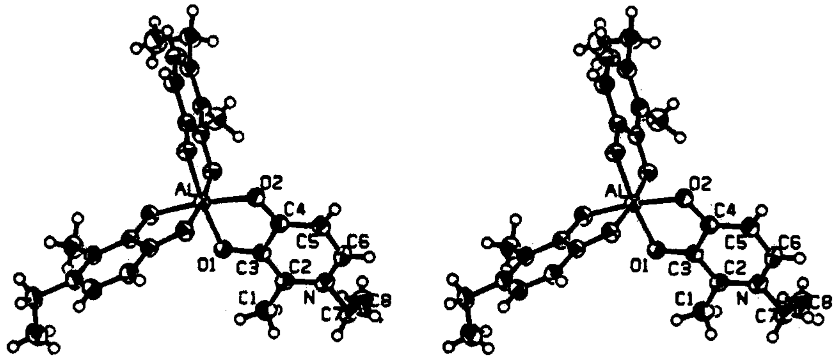

Figure 1. ORTEP stereoview of the tris(1-ethyl-3-hydroxy-2-methyl-4-pyridinonato)metal portion of the $AlL_3{\cdot}12H_2O$ complex. $GaL_3{\cdot}12H_2O$ is isostructural. The atom numbering shown is the same in all three structures.

of all the chelating O atoms; the type IA donor–acceptor interactions[16] throughout the structure. This discussion therefore focusses on specific features of these structures and examines the overall features of the structure based on studies of the N–H,[10] $N–CH_3$,[10] and $N–C_2H_5$ ligands and the six exoclathrate metal complexes.[1-4]

The bond lengths and angles in the uncomplexed $N–C_2H_5$ ligand HL compare well with those for its N–H and $N–CH_3$ congeners except for O(2)–C(4) and C(5)–C(6), which are shorter, and N–C(2), which is longer. The pyridinone ring is slightly nonplanar; the maximum deviation from the mean plane is 0.013 (3) Å, the distortion being toward an N–C(4) boat. N-alkylation results in a small intraannular bond angle at nitrogen (C(2)–N–C(6)), and the C(3)–C(4)–C(5) angle is compressed in all three compounds to a minimum of 114.3° in this structure. This compression is indicative of the strength of the C=O bond (O(2)–C(4), shortest in HL of the three analogues) and results in part from the lone pairs of electrons on the oxygen. The nitrogen coordination is planar within experimental error in all three compounds and the bond lengths indicate partial delocalization of the formal double bonds.

All the 3-hydroxy-2-methyl-4-pyridinones crystallize as centrosymmetric O—H···O=C hydrogen bonded dimeric units; in HL, these are separated from one another by normal van der Waals distances. In the packing of the dimeric units, the *N*-alkyl groups are staggered to allow the closest spacing of the pyridinone rings. Comparison of the $N–CH_3$ compound with HL ($N–C_2H_5$) shows that the *N*-ethyl group disrupts the stacking of the dimeric units; this is reflected in an increase in the volume of the unit cell (both compounds crystallized in the orthorhombic space group *Pbca*) from 1312 Å^3 in the $N–CH_3$ compound to 1628 Å^3 in HL. The HL crystal lattice appears to have been weakened by the steric requirements of the *N*-ethyl group (compare the lower melting point (205 vs 260 °C) and the greater water solubility (5-fold increase at 25 °C) of HL when compared to the N-methylated analogue).

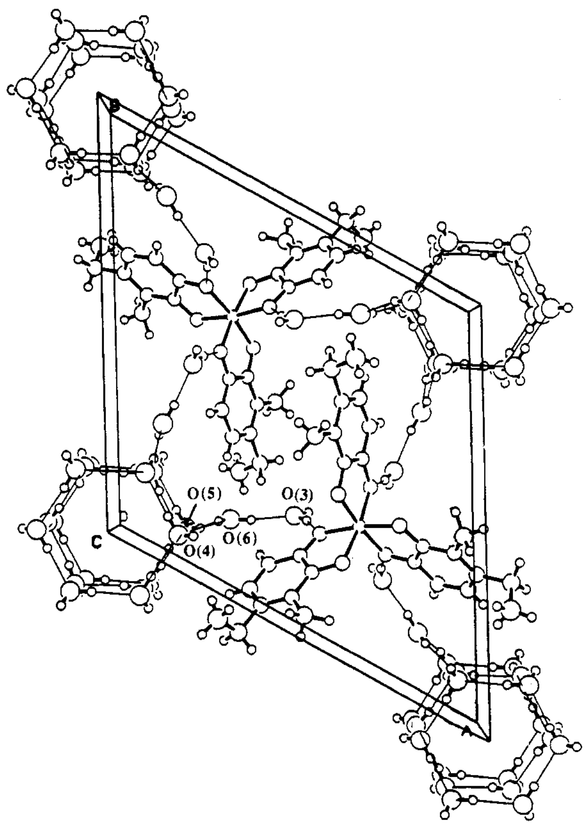

Figure 2. View down the *c* axis of the unit cell packing of the $AlL_3{\cdot}12H_2O$ complex. $GaL_3{\cdot}12H_2O$ is isostructural. Numbering for the nonchelating oxygen atoms is shown. O(5) is located directly below O(4).

The three-dimensional structure of the exoclathrate lattice is maintained in the Al and Ga dodecahydrate complexes of 1-ethyl-3-hydroxy-2-methyl-4-pyridinone. The 3-fold symmetry of the *fac* isomers (Figure 1) dictates an asymmetric unit consisting of one-third of a metal ion, one ligand, and four water molecules. The water molecules form hexagonal rings (O(4) and O(5)) that are hydrogen bonded to the chelating oxygen atoms of the complexes by bridging waters (O(3) and O(6) (Figure 2)). The water molecules do not coordinate the metal; they are structural waters and form a three-dimensional framework. That we have found

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(16) Jeffrey, G. A.; Takagi, S. *Acc. Chem. Res.* **1978**, *11*, 264.

it impossible to grow crystals of *any* exoclathrate complex from any solvent but water and wet ethanol attests to the importance of the lattice water.

The *fac*-ML$_3$ units of the Al and Ga complexes are isostructural (Figure 1). There appears to be an increase in delocalization in L$^-$ from that in HL, but this is mainly a change in only one bond, C(5)-C(6), that is the shortest for any of the structures solved (free ligands and metal complexes) in HL and was the longest in AlL$_3$—1.350 vs 1.380 Å. There is more delocalization in the C—O bonds of AlL$_3$ or GaL$_3$ than in those of HL or the complexes of its N-methylated analogue 3-hydroxy-1,2-dimethyl-4-pyridinone.[1-4] The difference between the two C–O bonds is 0.099 Å in HL and 0.020 and 0.024 Å in Al$_3$ and GaL$_3$, respectively. As in the 3-hydroxy-1,2-dimethyl-4-pyridinone complexes, a significant increase in double-bond delocalization occurs upon chelation.

Aside from the different *N*-alkyl groups, the complexes of 3-hydroxy-1,2-dimethyl-4-pyridinone and of 1-ethyl-3-hydroxy-2-methyl-4-pyridinone (HL) are isomorphous, with similar ligand bond lengths and angles. The chelate ring angles show a compression along the C_3 axis, and the M–O bond lengths are comparable. In the water network, some of the hydrogen bonds are slightly longer, but as was the case with the increased size of the metal ion, there is no evidence from the hydrogen-bond parameters that the water network is significantly affected by the additional methylene group in the ML$_3$ complexes. The rigidity of the water network that is responsible for the compression of the M–O–C bond angles along the C_3 axis can be seen in the length of c. For the 3-hydroxy-1,2-dimethyl-4-pyridinone complexes, c decreases as the metal radius increases (Al > Ga > Fe > In); an increase in the size of the *N*-alkyl substituent likewise causes a decrease in c, e.g. 0.050 Å in the Al complexes where R = CH$_3$ vs R = C$_2$H$_5$. It is the *ab* plane that the changes in the metal and ligand are accommodated by the water network. The result is an increase in a, for example a 0.242 Å increase for the In vs the Al complex of 3-hydroxy-1,2-dimethyl-4-pyridinone and a 0.573 Å increase for AlL$_3$ vs. its *N*–CH$_3$ analogue. As molecular size increases (because of either the metal *or* the ligand), the unit cell and the water network compresses along the c axis and spreads in the *ab* plane.

The packing diagram of AlL$_3$ (Figure 2) shows how the *N*-ethyl group fits into the hydrophobic core that is made up of one ligand from each of the two *fac*-ML$_3$ units in the cell. The flexibility of the structure in the *ab* plane is allowed by the large ring that encircles the core and consists of bridging waters, one side of the hexagonal water channels, and the M–O bonds in the *fac*-ML$_3$ units. The ligands in the core are separated by 3.5 ± 1 Å (normal van der Waals contacts). The points where the ligand carbon atoms approach the water rings, C(8)–O(5) and C(6)–O(6), are likewise separated by about 3.5 Å. To maintain this distance from the water network, the *N*-ethyl groups twist out of the ligand plane. The length of c(>6.8 Å) is considerably greater than van der Waals contact distances so there is ample space to accommodate the *N*-ethyl group without an increase in c and, therefore, without an increase in the length of the hydrogen bonds that determine this dimension. Increasing the length of the O–M–O portion of the inner ring pushes the water channels away from each other (increases a), but no strain is put on the water channels because they are connected through the *fac*-ML$_3$ unit and are not directly hydrogen bonded. The structure can be thought of as four rigid water columns held together by the more flexible *fac*-ML$_3$ units. An increase in the size of the metal simply pushes the water columns apart in the *ab* plane, and in the c direction where direct strain could be placed on water hydrogen bonds, the octahedral metal complexes are compressed before the hydrogen bonds are stretched. The unit cells of all the exoclathrate complexes are isomorphous except for the added methylene groups in ML$_3$. Our previous observation[3] of interchanged Λ and Δ isomers in the unit cell of the indium complex of 3-hydroxy-1,2-dimethyl-4-pyridinone was not a genuine structural difference but resulted from a different choice of crystallographic axes.

There is a growing family of tris(ligand)metal(III) complexes that present (when crystallized from water) appropriate conditions for the formation of the water channels in what was a previously unobserved hydrogen-bonding arrangement. This probably results by virtue of both the complex size and the hydrophobic core of the unit cell formed by the pairs of alkyl groups on the ligands from the two facially coordinated tris(ligand)metal(III) units. There is a clear alternation of hydrophilic and hydrophobic regions along the *ab* diagonals of the unit cell; no doubt this feature also contributes to the unique hydrogen bonding arrangement.

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Supplementary Material Available: Tables of anisotropic thermal parameters (Table SI), intramolecular distances and bond angles involving hydrogen atoms (Tables SII and SIII), least-squares planes (Table SIV), torsion angles (Table SV), and complete crystallographic data (Table IX) (13 pages); for the three compounds tables of observed and calculated structure factor amplitudes for each of the compounds (Tables SVI–SVIII) (41 pages). Ordering information is given on any current masthead page.