displaces zinc more easily than cadmium.[11] From the known order of metal-binding affinities for metallothionein, Cu > Cd > Zn, one can infer that gold will displace $Zn^{2+}$ in preference to $Cu^+$. Indeed, shortly after gold administration, the zinc content of metallothionein is decreased, while the copper and gold levels continue to increase.[7] The continued presence of zinc and copper in metallothionein suggests that $(TmSAu)_{20}$–Th does not form and that mixed-metal aurothioneins (e.g., Au,Cu,Zn–Th) are the principal in vivo forms.

**Note Added in Proof.** The kinetic study of the direct reaction of PAR (100–1500 $\mu$M) and $Zn_7Th$ (20 $\mu$M Zn) was reexamined under the same reaction conditions with a better spectrophotometer, which enabled us to observe an initial, fast step that was not previously resolved at PAR concentrations below 500 $\mu$M. This fast step is independent of the PAR concentration from 100 to 1500 $\mu$M and the first-order rate constant, $k_{1f}$, is $2.1 \times 10^{-3}$ s$^{-1}$. The fraction of the zinc ions reacting in the fast step was 0.03–0.07 for 100–500 $\mu$M PAR and never exceeded 0.17 at the highest concentration (1500 $\mu$M). Thus it corresponds, at most, to one of the seven zinc ions in MT. Thus, the direct PAR reaction consists of two steps, the fast step described here and the slow step described in the Results section:

$$\text{rate}_f = k_{1f}[Zn] \qquad \text{rate}_s = k_{1s}[Zn] + k_{2s}[PAR][Zn]$$

The contribution of the direct PAR reactions to the overall reaction in the presence of AuSTm was recalculated by using these rate constants for the direct reaction and the average rate constants for the AuSTm reaction from Table II, here designated $k_{f,Au}$ and $k_{s,Au}$:

$$\text{fraction} = \frac{\Sigma k_{PAR}}{\Sigma k_{PAR} + \Sigma k_{Au}} =$$
$$\frac{(1/7)k_{1f} + k_{1s} + k_{2s}[PAR]}{(1/7)k_{1f} + k_{1s} + k_{2s}[PAR] + k_{f,Au} + k_{s,Au}} = 0.011$$

Although the relative magnitudes of $k_{1f}$ and $k_{f,Au}$ suggest that a substantial amount of $Zn^{+2}$ might be extracted directly by PAR, the small fraction of the zinc reacting in the $k_{1f}$ step (taken as $^1/_7$ of the total in the calculation, renders it insignificant. Thus, the claim in the text that only about 1% of the zinc is directly extracted by PAR remains valid, despite the existence of the $k_{1f}$ step that was not known to us at that time.

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# Aluminum Citrate: Isolation and Structural Characterization of a Stable Trinuclear Complex

Timothy L. Feng, Patrick L. Gurian, Matthew D. Healy, and Andrew R. Barron*

The complex anion $[Al_3(H_{-1}Cit)_3(OH)(H_2O)]^{4-}$ has been isolated from the reaction of $Al(NO_3)_3\cdot 9H_2O$ with citric acid ($H_3Cit$) in aqueous solution between pH 7 and 9. The complex has been characterized by $^1$H, $^{13}$C, and $^{27}$Al NMR spectroscopy and X-ray crystallography. The complex $[NH_4]_5[Al_3(H_{-1}Cit)_3(OH)(H_2O)][NO_3]\cdot 6H_2O$ ($C_{18}H_{47}Al_3N_6O_{32}$) crystallizes in the monoclinic space group $P2_1/a$ with the following crystal parameters: $a$ = 17.289 (5) Å, $b$ = 13.210 (6) Å, $c$ = 17.705 (5) Å, $\beta$ = 115.34 (2)°, $Z$ = 4. The data was refined by using 5301 reflections to $R$ = 8.46, $R_w$ = 9.48. The complex anion consists of a trimeric $Al_3O_4$ core with each citrate ligand coordinated to two or more aluminum atoms. Variable-pH $^{27}$Al NMR has been used to study the degradation of the trimer at low pH.

During the past decade, an ever increasing volume of evidence has been presented to associate aluminum with a variety of neurotoxic conditions.[1] Increased aluminum levels have been detected in patients suffering from Alzheimer's disease[2] as well as those undergoing dialysis treatment for chronic renal failure.[3] The toxicity of $Al^{3+}$ raises questions concerning the possible route of its absorption into the body and its binding modes after ingestion. It has been suggested that citric acid ($H_3Cit$), which occurs at about 0.1 mM in blood plasma, is the most likely small molecule plasma binder of $Al^{3+}$.[4]



$H_3Cit$
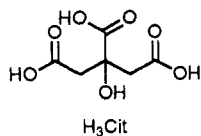
Citrate binding of $Al^{3+}$, in aqueous solution, has been described in several recent studies[5–8] where agreement is limited to acknowledging the formation of the complexes $[Al(HCit)]^+$ and $Al(Cit)$ between pH 1 and 3. A definitive study by Öhman and co-workers[9] covering all the points of the speciation suggests that a stable trimeric aluminum citrate complex is the major species in an equimolar Al:Citric acid solution between pH 4 and 9. The trimer was formulated as either $[Al_3(Cit)_3(OH)_4(H_2O)]^{4-}$ or $[Al_3(H_{-1}Cit)_3(OH)(H_2O)_5]^{4-}$ and was proposed to be structurally similar to the magnesium citrate decahydrate complex.[10]

The tendency of aluminum alkoxide and carboxylate compounds to maximize the aluminum coordination number by associating to give aggregates containing tetrahedral and octahedral centers is well documented.[11] The aim of the present study is to investigate the possibility of polynuclear aluminum citrate complexes from aqueous solution.

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(10) Johnson, C. D. *Acta Crystallogr.* **1965**, *18*, 1004.
(11) Bradley, D. C. *Adv. Chem. Ser.* **1959**, No. 23, 10.
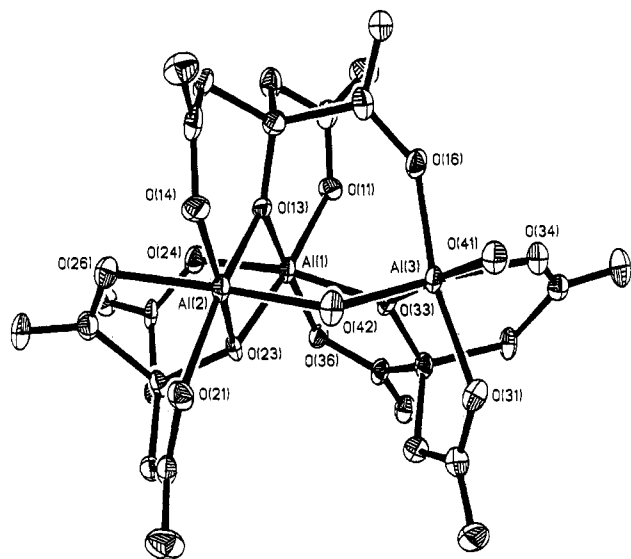
**Figure 1.** View of the $[Al_3(H_{-1}Cit)_3(OH)(H_2O)]^{4-}$ anion showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels. Citrate hydrogen atoms have been omitted for clarity.
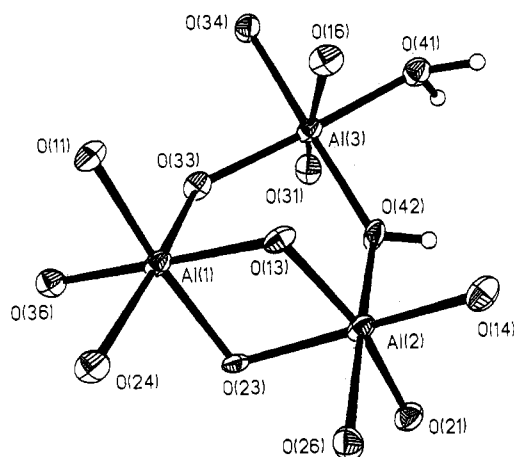


**Figure 2.** Partial coordination sphere of the aluminum core in the $[Al_3(H_{-1}Cit)_3(OH)(H_2O)]^{4-}$ anion. Thermal ellipsoids show 50% probability levels.

## Results and Discussion

Neutralization of an equimolar solution of aluminum nitrate and citric acid with aqueous ammonia yields, on slow evaporation of the solvent, colorless crystals of the ammonium salt of the trimeric anionic complex $[Al_3(H_{-1}Cit)_3(OH)(H_2O)]^{4-}$, which is surrounded by a hydrogen-bonded network of six water molecules, five ammonium cations, and a nitrate anion. The structure of the $[Al_3(H_{-1}Cit)_3(OH)(H_2O)]^{4-}$ anion and the atom-numbering scheme are shown in Figure 1. Selected bond lengths and angles are given in Table I.

The core of the anionic complex is composed of a bicyclic aluminum–oxygen framework consisting of fused four- and six-membered rings (Figure 2). All three aluminum atoms exhibit distorted octahedral coordination geometry. The $Al_3O_4$ core in $[Al_3(H_{-1}Cit)_3(OH)(H_2O)]^{4-}$ (1) is similar to the $Al_4O_6$ core observed for $\{[N(CH_2CH_2O)_3]Al_2Me_3\}_2$ (2).[12] At present these two
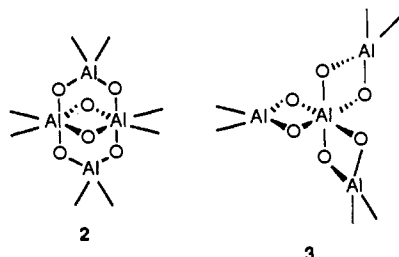


**Table I.** Selected Bond Distances (Å) and Angles (deg) for $[NH_4]_5[Al_3(H_{-1}Cit)_3(OH)(H_2O)][NO_3]\cdot6H_2O$

| Bond Distances | | | |
|---|---|---|---|
| Al(1)–O(11) | 1.855 (5) | Al(1)–O(13) | 1.851 (4) |
| Al(1)–O(23) | 1.892 (5) | Al(1)–O(24) | 1.930 (5) |
| Al(1)–O(33) | 1.930 (5) | Al(1)–O(36) | 1.896 (4) |
| Al(2)–O(42) | 1.832 (5) | Al(2)–O(13) | 1.879 (5) |
| Al(2)–O(14) | 1.848 (4) | Al(2)–O(21) | 1.907 (5) |
| Al(2)–O(23) | 1.909 (4) | Al(2)–O(26) | 1.934 (5) |
| Al(3)–O(41) | 1.935 (5) | Al(3)–O(42) | 1.849 (4) |
| Al(3)–O(16) | 1.845 (4) | Al(3)–O(31) | 1.914 (5) |
| Al(3)–O(33) | 1.883 (5) | Al(3)–O(34) | 1.917 (4) |

| Bond Angles | | | |
|---|---|---|---|
| O(11)–Al(1)–O(13) | 93.2 (2) | O(13)–Al(1)–O(23) | 78.7 (2) |
| O(11)–Al(1)–O(23) | 171.6 (2) | O(11)–Al(1)–O(24) | 90.9 (2) |
| O(13)–Al(1)–O(24) | 100.8 (2) | O(23)–Al(1)–O(24) | 88.9 (2) |
| O(13)–Al(1)–O(33) | 90.7 (2) | O(11)–Al(1)–O(33) | 93.5 (2) |
| O(24)–Al(1)–O(33) | 167.4 (2) | O(23)–Al(1)–O(33) | 88.4 (2) |
| O(11)–Al(1)–O(36) | 90.4 (2) | O(13)–Al(1)–O(36) | 172.8 (2) |
| O(23)–Al(1)–O(36) | 97.9 (2) | O(24)–Al(1)–O(36) | 85.4 (2) |
| O(33)–Al(1)–O(36) | 82.8 (2) | O(42)–Al(2)–O(13) | 90.3 (2) |
| O(13)–Al(2)–O(14) | 95.4 (2) | O(42)–Al(2)–O(14) | 91.9 (2) |
| O(42)–Al(2)–O(21) | 89.9 (2) | O(13)–Al(2)–O(21) | 166.5 (2) |
| O(14)–Al(2)–O(21) | 98.2 (2) | O(13)–Al(2)–O(23) | 77.6 (2) |
| O(42)–Al(2)–O(23) | 96.1 (2) | O(21)–Al(2)–O(23) | 88.9 (2) |
| O(14)–Al(2)–O(23) | 169.4 (2) | O(42)–Al(2)–O(26) | 177.3 (2) |
| O(13)–Al(2)–O(26) | 92.4 (2) | O(14)–Al(2)–O(26) | 88.2 (2) |
| O(21)–Al(2)–O(26) | 87.4 (2) | O(23)–Al(2)–O(26) | 84.1 (2) |
| O(41)–Al(3)–O(42) | 90.8 (2) | O(41)–Al(3)–O(16) | 85.9 (2) |
| O(42)–Al(3)–O(16) | 97.1 (2) | O(41)–Al(3)–O(31) | 82.1 (2) |
| O(42)–Al(3)–O(31) | 89.5 (2) | O(16)–Al(3)–O(31) | 166.3 (2) |
| O(41)–Al(3)–O(33) | 175.9 (2) | O(42)–Al(3)–O(33) | 91.7 (2) |
| O(16)–Al(3)–O(33) | 97.1 (2) | O(31)–Al(3)–O(33) | 94.6 (2) |
| O(41)–Al(3)–O(34) | 87.4 (2) | O(42)–Al(3)–O(34) | 175.5 (2) |
| O(16)–Al(3)–O(34) | 86.8 (2) | O(31)–Al(3)–O(34) | 86.2 (2) |
| O(33)–Al(3)–O(34) | 89.9 (2) | | |

compounds are the only examples of fused polycyclic $Al_xO_y$ cores as compared to the more commonly observed nonfused core (3).

The coordination sphere of Al(1) consists of the hydroxy moiety and one carboxylate oxygen from each of the three citrate ligands. The hydroxy oxygens act as bridges to the other aluminum atoms, two to Al(2) [O(13), O(23)] and one to Al(3) [O(33)]. The three terminal oxygen atoms on Al(2) are from carboxylate groups [O(14), O(21), O(26)]. The bridging oxygen between Al(2) and Al(3) does not, however, originate from a citrate ligand but is a hydroxide ligand [O(42)]. The coordination around Al(3) consists of three terminal citrate carboxylate oxygens [O(16), O(31), O(34)], a bridging citrate hydroxyl oxygen [O(33)], a bridging hydroxide [O(42)], and a terminal water molecule [O(41)].

The aluminum–oxygen distances [1.832 (5)–1.935 (5) Å, average 1.888 (5) Å] do not differ significantly between terminal and bridging oxygens and are within the expected range 1.8–2.0 Å.[13] The reason for the variation of Al–O distance within the complex is presumably due to steric strain involved in coordination of the citrate to more than one aluminum atom.

The three independent citrate ions are distinct in their coordination to the aluminum atoms. Citrate 1 is coordinated to all three aluminums. The hydroxyl oxygen bridges Al(1) and Al(2), the two terminal carboxylate groups coordinate to Al(1) and Al(2), and the central carboxylate group is bonded to Al(3). In this conformation, the terminal carboxylates are nearly coplanar with the hydroxyl group. Such a conformation has been observed previously in $[Ni_4(H_{-1}Cit)_3(OH)(H_2O)]$.[14] As with citrate 1 the hydroxyl group of citrates 2 and 3 act as bridges between two aluminum atoms. Unlike citrate 1, however, citrates 2 and 3 only bridge two aluminum atoms. Citrate 2 coordinates to Al(2) via one terminal carboxylate as well as the central carboxylate and

(12) Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 398.
(13) See, for example: (a) Zaworotko, M. J.; Rogers, R. D.; Atwood, J. L. *Organometallics* **1982**, *1*, 1179. (b) Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 302.
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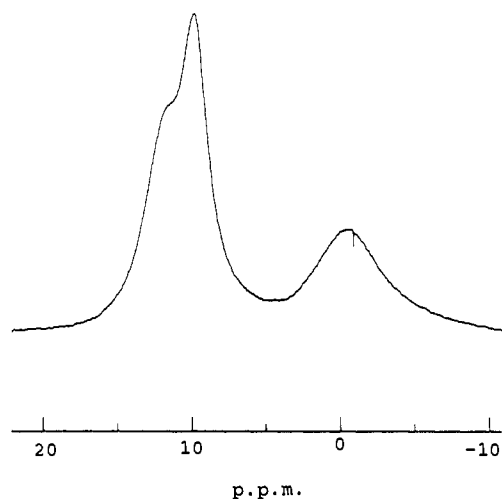
**Figure 3.** $^{27}$Al NMR spectrum of [NH$_4$]$_4$[Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)].

to Al(1) by the other terminal carboxylate. Citrate 3 on the other hand coordinates to Al(3) via both terminal carboxylates with the central carboxylate bonded to Al(1).

The presence of three distinct aluminum and citrate environments is conserved in solution (3 < pH < 9), suggesting that the [Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)]$^{4-}$ anion is not fluxional in solution. The $^{27}$Al NMR spectrum of [NH$_4$]$_4$[Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)] consists of three singlets (Figure 3). Although it is difficult to assign the peaks to individual aluminum atoms, a tentative assignment can be made on the basis of the line width of each peak, which is related to the local symmetry around each aluminum nucleus.[15] Thus, the peak at 0.2 ppm is assigned to Al(3) while the peaks at 10.7 and 12.6 ppm are due to Al(1) and Al(2). The retention of the trimeric structure in solution is also confirmed by the observation of three distinct groups of citrate resonances in the $^{13}$C NMR spectrum (see the Experimental Section). Both $^{27}$Al and $^{13}$C NMR spectra remain constant up to 60 °C.

The complex has been crystallized from solution over a range 7 > pH > 9 with the only variable being the number of water molecules and (NH$_4$)(NO$_3$) groups present in the crystal lattice. All $^{27}$Al and $^{13}$C NMR spectroscopic data remain constant between samples.

The hydrolysis behavior of the complex anion can be monitored by variable-pH $^{27}$Al NMR spectroscopy. The variable-pH $^{27}$Al NMR spectra for [Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)]$^{4-}$ are identical with those obtained for an equimolar mixture of Al(NO$_3$)$_3$ and citric acid in the same pH range. Acid hydrolysis occurs below pH 3.0, resulting in a broadening and eventual coalescence of the three resonances for [Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)]$^{4-}$, to give a broad peak (6.6 ppm) due to [Al(Cit)(H$_2$O)$_x$] and/or [Al(HCit)(H$_2$O)$_y$]$^+$ and a sharp peak (0.0 ppm) due to [Al(H$_2$O)$_6$]$^{3+}$ (Figure 4). As the solution is acidified further, the uncoordinated aluminum species predominates. The $^{27}$Al NMR spectra suggest that even at pH 0.3 a significant amount of the mononuclear aluminum/citric acid complex is present. A minor constituent is observed at 21.4 ppm between pH 2.0 and 3.7. We assign this to the dicitrate species [Al(Cit)$_2$]$^{3-}$ that has been proposed by a number of groups.[5-9] The hydrolysis of aluminum/3-hydroxy-4-pyridone complexes has been shown to be time dependent (up to 14 days).[16] We have found that equilibrium on hydrolysis of [Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)]$^{4-}$ is attained within 18 h at room temperature.

The cyclic voltammogram of a pH 7 buffered solution of [NH$_4$]$_4$[Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)] shows a reversible one-electron-reduction wave at −0.62 V consistent with the deprotonation of a water of coordination and is comparable to the reduction wave
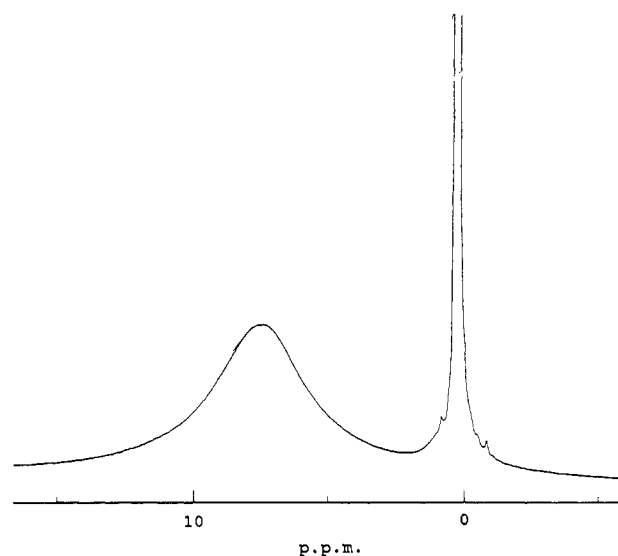
(15) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: London, 1978.
(16) Nelson, W. O.; Karpishin, T. B.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1988**, *27*, 1045.



**Figure 4.** $^{27}$Al NMR spectra of Al$^{3+}$/citric acid at pH 0.3.

**Table II.** Summary of X-ray Diffraction Data

| | |
|---|---|
| formula | C$_{18}$H$_{47}$Al$_3$N$_6$O$_{32}$ |
| space group | $P2_1/a$ |
| $a$, Å | 17.289 (5) |
| $b$, Å | 13.210 (6) |
| $c$, Å | 17.705 (5) |
| $\beta$, deg | 115.34 (2) |
| $V$, Å$^3$ | 3654 (2) |
| $Z$ | 4 |
| $D$(calcd), g/cm$^3$ | 1.651 |
| cryst dimens, mm | 0.51 × 0.36 × 0.42 |
| temp, K | 181 |
| radiation | Mo K$\alpha$ (0.710 73 Å, graphite monochromator) |
| $\mu$, cm$^{-1}$ | 2.15 |
| $2\theta$ limits | 4.0–55.0 |
| no. of data collcd | 8053 |
| no. of unique data | 7474 |
| no. of obsd data | 5301 |
| $R$ | 0.0764 |
| $R_w$ | 0.0850 |
| GOF | 2.13 |
| final residual, e Å$^{-3}$ | 2.10 |

observed for aluminum nitrate under similar conditions (−0.61 V). A second irreversible reduction wave (−0.86 V) is consistent with the structural rearrangement of the Al$_3$O$_4$ core, proposed by Ohman[9] to occur for the formation of the trimeric anion [Al$_3$(H$_{-1}$Cit)$_3$(OH)$_4$]$^{7-}$, from [Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)]$^{4-}$ at high pH.

**Conclusion**

The isolation of the [Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)]$^{4-}$ anion represents the first direct proof of both the existence of polynuclear complexes, of the type proposed by Öhman and co-workers,[9] and the deprotonation and coordination of the citrate hydroxy group. The structural characterization of [Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)]$^{4-}$ has assisted in the assignment of the complex $^{27}$Al NMR spectrum of the Al$^{3+}$/citric acid system over the pH range 0.3–9.0.

Although it is uncertain that polynuclear aluminum/citrate complexes would be present at a total Al concentration of 10$^{-6}$ M, a value typically found in blood plasma, or at the much greater citrate to Al ratio that favors formation of other than equimolar complexes, it is clear that such species are present at higher concentration (>10$^{-4}$ M) and may exist for other polycarboxylic acids.

**Experimental Section**

Reagent grade Al(NO$_3$)$_3$·9H$_2$O (Mallinckrodt) and citric acid (Aldrich) were used without further purification. Microanalyses were performed by Oneida Research Services, Whitesboro, NY. NMR spectra of [NH$_4$]$_4$[Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)], in D$_2$O, were recorded on

**Table III.** Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($10^3 \times$ Å$^2$) of the Non-Hydrogen Atoms in $[NH_4]_5[Al_3(H_{-1}Cit)_3(OH)(H_2O)][NO_3]\cdot6H_2O$

| | $x$ | $y$ | $z$ | $U(eq)^a$ |
|---|---|---|---|---|
| Al(1) | 5802 (1) | 608 (1) | 3052 (1) | 139 (6) |
| Al(2) | 7088 (1) | −429 (1) | 2688 (1) | 143 (6) |
| Al(3) | 7300 (1) | 2093 (1) | 2806 (1) | 138 (6) |
| O(41) | 8414 (3) | 2485 (3) | 2895 (3) | 187 (15) |
| O(42) | 7437 (3) | 804 (3) | 2474 (3) | 176 (16) |
| O(11) | 5860 (3) | 1242 (3) | 4010 (2) | 177 (15) |
| O(12) | 6393 (3) | 1695 (3) | 5336 (3) | 280 (18) |
| O(13) | 6915 (3) | 135 (3) | 3577 (2) | 141 (13) |
| O(14) | 5203 (3) | −828 (3) | 3333 (3) | 185 (15) |
| O(15) | 9386 (3) | −1082 (3) | 4480 (3) | 230 (16) |
| O(16) | 7846 (3) | 1867 (3) | 3943 (3) | 188 (15) |
| O(17) | 8691 (3) | 1352 (3) | 5228 (3) | 245 (17) |
| C(11) | 6415 (4) | 1144 (4) | 4791 (4) | 184 (21) |
| C(12) | 7081 (4) | 300 (4) | 4977 (4) | 213 (23) |
| C(13) | 7524 (4) | 240 (4) | 4412 (3) | 160 (19) |
| C(14) | 8136 (4) | −692 (4) | 4666 (4) | 188 (21) |
| C(15) | 8613 (4) | −876 (4) | 4128 (4) | 185 (21) |
| C(16) | 8072 (4) | 1217 (4) | 4529 (4) | 181 (21) |
| O(21) | 6988 (3) | −916 (3) | 1636 (3) | 178 (15) |
| O(22) | 6324 (3) | −1066 (4) | 258 (3) | 294 (19) |
| O(23) | 5892 (3) | −133 (3) | 2179 (3) | 143 (14) |
| O(24) | 5184 (3) | −515 (3) | 3229 (3) | 194 (16) |
| O(25) | 4154 (3) | −1653 (3) | 2836 (3) | 234 (17) |
| O(26) | 6721 (3) | −1755 (3) | 2866 (3) | 187 (15) |
| O(27) | 5579 (3) | −2761 (3) | 2340 (3) | 251 (18) |
| C(21) | 6308 (4) | −1029 (4) | 946 (4) | 192 (22) |
| C(22) | 5444 (4) | −1148 (4) | 961 (4) | 191 (21) |
| C(23) | 5451 (4) | −1040 (4) | 1824 (3) | 150 (19) |
| C(24) | 4552 (4) | −1014 (4) | 1781 (3) | 164 (20) |
| C(25) | 4596 (4) | −1065 (4) | 2650 (4) | 180 (22) |
| C(26) | 5946 (4) | −1945 (4) | 2385 (4) | 200 (22) |
| O(31) | 6946 (3) | 2557 (3) | 1683 (3) | 194 (16) |
| O(32) | 6161 (3) | 2596 (3) | 327 (3) | 242 (17) |
| O(33) | 6183 (3) | 1793 (3) | 2670 (2) | 150 (14) |
| O(34) | 7157 (3) | 3467 (3) | 3071 (3) | 184 (15) |
| O(35) | 6434 (3) | 4830 (3) | 3095 (3) | 267 (18) |
| O(36) | 4706 (3) | 1182 (3) | 2422 (3) | 168 (15) |
| O(37) | 3998 (3) | 2483 (3) | 1658 (3) | 189 (15) |
| C(31) | 6230 (4) | 2474 (4) | 1046 (4) | 174 (20) |
| C(32) | 5465 (4) | 2190 (4) | 1182 (4) | 180 (20) |
| C(33) | 5508 (4) | 2378 (4) | 2056 (3) | 154 (20) |
| C(34) | 5603 (4) | 3506 (4) | 2306 (4) | 224 (23) |
| C(35) | 6454 (4) | 3954 (4) | 2855 (4) | 155 (20) |
| C(36) | 4681 (4) | 1999 (4) | 2035 (4) | 169 (20) |
| N(1) | 6141 (4) | 5838 (4) | 586 (4) | 346 (28) |
| O(3) | 6474 (5) | 6563 (5) | 1073 (4) | 599 (31) |
| O(4) | 6048 (4) | 5007 (5) | 871 (4) | 530 (29) |
| O(5) | 5879 (4) | 5965 (4) | −165 (3) | 383 (22) |
| O(6) | 9966 (3) | 1849 (4) | 3914 (3) | 299 (18) |
| O(7) | 8604 (3) | 482 (3) | 1726 (3) | 256 (18) |
| O(2) | 7526 (4) | −21 (4) | 32 (3) | 399 (23) |
| O(8) | 8877 (3) | 4451 (3) | 3902 (3) | 310 (20) |
| O(9) | 3394 (3) | 6885 (3) | 1615 (3) | 259 (18) |
| N(10) | 4519 (4) | 5993 (4) | 932 (4) | 250 (21) |
| N(8) | 10048 (4) | 774 (4) | 6821 (3) | 231 (20) |
| N(6) | 7419 (4) | 7206 (4) | −11 (3) | 271 (21) |
| N(4) | 2510 (4) | −1304 (4) | 2897 (4) | 277 (22) |
| O(1) | 7871 (4) | 4569 (5) | 1664 (4) | 485 (27) |
| N(3) | 5322 (4) | −1836 (4) | 4682 (3) | 244 (20) |

$^a$ Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Bruker AM-250 ($^1$H and $^{13}$C) and Bruker WM-300 ($^{27}$Al) spectrometers [$\delta$ in parts per million relative to external SiMe$_4$ ($^{13}$C) and external Al[(H$_2$O)$_6$]$^{3+}$ ($^{27}$Al)]. Cyclic voltammetry experiments were carried out with a Princeton Applied Research (PAR) Model 173 potentiostat, a PAR Model 175 universal programmer and Houston Instruments Model 2000 X-Y recorder. Measurements were made on $10^{-4}$ M solutions in a pH 7 buffered solution. pH measurements were made with a Corning 245 pH meter.

**$[NH_4]_4[Al_3(H_{-1}Cit)_3(OH)(H_2O)]$.** In a representative experiment, aluminum nitrate Al(NO$_3$)$_3$·9H$_2$O (18.76 g, 0.05 mol) was added to citric acid, C$_6$H$_8$O$_7$ (9.60 g, 0.05 mol), in warm distilled water (200 mL, 60 °C). NH$_4$OH solution was added dropwise until the solution equilibrated at pH 7.5. The solution was stirred for 4 h and then concentrated, in vacuo, to 50 mL while heating to 80 °C. Cooling to room temperature resulted in the slow crystallization of large colorless crystals. Yield: 60–70%. Anal. Calcd for C$_{18}$H$_{53}$Al$_3$N$_8$O$_{36}$: C, 20.8; H, 5.11; N, 10.8. Found: C, 21.0; H, 4.83; N, 10.2. Crystals suitable for X-ray crystallography were obtained by slow evaporation in air of a pH 9 solution. Anal. Calcd for C$_{18}$H$_{47}$Al$_3$N$_6$O$_{32}$: C, 23.0; H, 5.00; N, 8.94. Found: C, 23.0; H, 4.76; N, 9.02.

NMR (D$_2$O, $\delta$): $^1$H, 5.96 (1 H, br s, OH), 4.71 (12 H, m, −CH$_2$−); $^{13}$C, 182.0, 181.7, 180.0 [OC(CO$_2$)(CH$_2$CO$_2$)$_2$], 177.6, 177.2, 176.9, 176.8, 176.7, 176.4 [OC(CO$_2$)(CH$_2$CO$_2$)$_2$], 75.1, 74.9, 72.8 [OC(CO$_2$)(CH$_2$CO$_2$)$_2$], 45.9, 45.7, 44.7, 43.4, 42.5, 41.5 [OC(CO$_2$)(CH$_2$CO$_2$)$_2$]; $^{27}$Al, 12.6 ($W_{1/2}$ = 205 Hz), 10.7 ($W_{1/2}$ = 200 Hz), 0.2 ($W_{1/2}$ = 339 Hz).

**Variable-pH $^{27}$Al NMR Spectroscopy.** To a D$_2$O solution of either an equimolar mixture of Al(NO$_3$)$_3$·9H$_2$O and citric acid or [NH$_4$]$_4$[Al$_3$-(H$_{-1}$Cit)$_3$(OH)(H$_2$O)] was added a known volume of standard NH$_4$OH or HNO$_3$ solutions. The solution was allowed to equilibrate for 18 h, at 25 °C, and the pH measured before the NMR spectra were collected.

**Crystallography.** A crystal data summary is given in Table II; fractional atomic coordinates for [Al$_3$(H$_{-1}$Cit)$_3$(OH)(H$_2$O)]$^{4-}$ are given in Table III. X-ray data were collected on a Nicolet R3m/V four-circle diffractometer equipped with a LT-1 low-temperature device. Data collection was controlled with the Nicolet P3 program. The unit cell was indexed by using 2$\theta$ reflections obtained from a rotation photograph. A lattice determination using both the P3 program and XCELL suggested a monoclinic cell. Examination of the axial photographs confirmed this assignment. Systematic absences were consistent with the space group $P2_1/a$. The final unit cell parameters were obtained by a least-squares refinement of 50 selected reflections in the range 15° < 2$\theta$ < 30°.

A total of 8053 reflections were collected in the range 4° < 2$\theta$ < 55°. Of these 7474 were unique reflections and 5301 with $F_o > 6\sigma(F_o)$ were used in the structure solution. The intensities of three check reflections were measured every 60 reflections; the intensities did not vary significantly during the data collection. A semiempirical absorption correction based on six reflections in the range 8 < 2$\theta$ < 40°, was applied by using the program PSICOR. Lorentz and polarization corrections were applied to the data. The SHELXTL-PLUS series of programs was used for all calculations.[17]

Use of direct methods readily revealed the positions of the aluminum atoms. Standard difference map techniques were used to find the remaining non-hydrogen atoms. The crystallographic identification of H$_2$O and NH$_4$$^+$ was assigned on the basis of the atom thermal parameters in conjunction with the elemental analysis. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed all of the hydrogen atoms associated with the aluminum citrate anion; however, not all of the hydrogen atoms associated with the ammonium cations and the waters of solvation were located, so they were omitted from the final refinement. Refinement was performed to convergence ($\Delta/\delta$(max) < 0.001) with this model. The weighting scheme was $w = [\sigma^2(F) + 0.00179F^2]^{-1}$.

The only significant peaks in the final difference map were in positions consistent with hydrogens on the NH$_4$$^+$ and H$_2$O moieties.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, complete bond lengths and angles, and hydrogen atom parameters (6 pages); a table of calculated and observed structure factors (27 pages). Ordering information is given on any current masthead page.

(17) *SHELXTL-PLUS Users Manual*; Nicolet Instrument Corp.: Madison, WI, 1988.