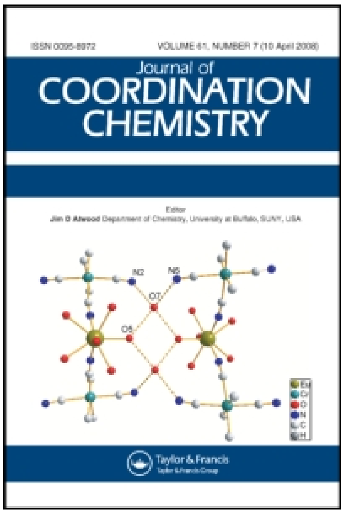

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# SYNTHESES, STRUCTURES AND SPECTROSCOPIC PROPERTIES OF NICKEL(II) CITRATO COMPLEXES, (NH4)$_2$[Ni(Hcit)(H$_2$O)$_2$]$_2$-2H$_2$O AND (NH$_4$)$_4$[Ni(Hcit)2]-2H$_2$O

Zhao-Hui Zhou[a]; Yi-Ji Lin[a]; Hong-Bin Zhang[a]; Guo-Dong Lin[a]; Khi-Rui Tsai[a]
[a] Department of Chemistry, State Key Laboratory for Physical Chemistry, Xiamen University, Xiamen, China

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# SYNTHESES, STRUCTURES AND SPECTROSCOPIC PROPERTIES OF NICKEL(II) CITRATO COMPLEXES, $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2\cdot 2H_2O$ AND $(NH_4)_4[Ni(Hcit)_2]\cdot 2H_2O$

ZHAO-HUI ZHOU *, YI-JI LIN, HONG-BIN ZHANG, GUO-DONG LIN
AND KHI-RUI TSAI

*Department of Chemistry, State Key Laboratory for Physical Chemistry, Xiamen University, 361005 Xiamen, China*

*(Received 30 August 1996)*

Dimeric ammonium diaquocitratonickelate (II) dihydrate $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2\cdot 2H_2O$, **1**, and its sodium and potassium salts, as well as ammonium dicitratonickelate (II) dihydrate $(NH_4)_4[Ni(Hcit)_2]\cdot 2H_2O$, **2**, ($H_4$cit = citric acid) have been synthesized and characterized by spectroscopic methods. The crystal structures of **1** and **2** were determined by X-ray methods. Compound **1** is triclinic, space group $P\bar{1}$ with $a = 6.4071(7)$, $b = 9.4710(7)$, $c = 9.6904(5)$ Å, $\alpha = 105.064(5)$, $\beta = 91.992(7)$, $\gamma = 89.334(8)°$, $V = 567.5(1)$ Å$^3$, $Z = 1$, $R = 0.037$ for 1714 observed reflections. The structure consists of centrosymmetric dimers, $[Ni(Hcit)(H_2O)_2]_2^{2-}$. The principal Ni—O dimensions are Ni—O(hydroxy), 2.074(2)Å, Ni—O(α-carboxy), 2.020(3)Å, Ni—O(β-carboxy), 2.031(2), 2.037(2)Å, Ni—O(water), 2.065(2), 2.072(3)Å. Compound **2** crystallizes in the monoclinic space group $P\,2_1/a$ with $a = 9.361(1)$, $b = 13.496(1)$, $c = 9.4238(7)$Å, $\beta = 115.475(6)°$, $V = 1074.9(3)$Å$^3$, $Z = 2$, $R = 0.052$ for 1507 observed reflections. The two terdentate citrato ligands coordinate symmetrically to one nickel *via* hydroxyl, α- and β-carboxylato oxygens and the remaining acetato groups are bonded through strong hydrogen bonds with the hydroxy group of another dicitrato nickel anion [2.526(6)Å]. The principal Ni—O dimensions are: Ni—O(hydroxy), 2.021(3)Å, Ni—O (α-carboxy), 2.038(3)Å, Ni—O(β-carboxy), 2.072(3)Å. Nickel atoms in the two compounds have octahedral geometry. The two compounds can be transformed easily by reaction with ammonium citrate or nickel chloride.

*Keywords:* nickel; citric acid; citrate; X-ray structure

## INTRODUCTION

Citric acid ($C_6H_8O_7 = H_4$cit) is of widespread importance in biological systems and has a number of key physiological functions.[1] Most of these depend on the chelating

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* Author for correspondence.

ability of citrate anions. Above pH 8.0, the $Hcit^{3-}$ is the predominant form, and deprotonation of the hydroxyl group is accelerated by its bonding with metal ions such as V(V), Mo(VI) and W(VI).[2-4] In these metal complexes, the tetraionized species is apparently formed at pH 5–7, while for Ni(II) complex, it is not formed below pH 9.[5,6] For several New Caledonian species of *Sebertia, Hybanthus* and *Homalium* containing nickel, citrate is involved in complex formation, where electrophoretic studies indicate that the complex is negatively charged.[7] In fact, nickel is recognized as an essential trace element for bacteria, plants, animals and humans,[8] while its role remains largely undefined. In an entirely different mode, citric acid is used as a chelating agent in electroplating baths for various Ni alloys,[9] and biodegredation of waste soluble nickel citrates generated from this process has been reported recently.[10,11] Moreover, the citrate method has important potential in the preparation of well-defined and high surface area particles,[12] such as for Ni-based catalysts for hydrogenation or the partial oxidation of methane, in which $MNiO_2$ (M = $Mg^{2+}$, $Ca^{2+}$) or rare earth mixed oxides can be prepared from their corresponding nickel citrate precursors.[13,14]

To now, there are only two well-characterized crystal structures of nickel(II) citrate complexes reported in literature. One is $\{[N(CH_3)_4]_5[Ni(II)_4(cit)_3(OH)(H_2O)]\cdot 18H_2O\}_2$ formed at pH 9.2,[5] and the other is $K_2[Ni(Hcit)(H_2O)_2]_2\cdot 4H_2O$ formed at pH 5.[15] Hedwig *et al.*,[16] reported potentiometric and visible spectroscopic studies of various complexes formed between nickel(II) ions and citric acid in dilute solution and proposed four species NiHL, $NiH_2L$, $NiH_3L^+$ and $Ni(HL)_2^{4-}$ (L = cit). In the meantime, there was a report on solution studies of polynuclear species in the nickel(II) citrate system, including $Ni_4(OH)_4(HL)_3^{5-}$ $Ni_4(OH)(H_2L)_3^{5-}$, $Ni(HL)_2^{4-}$ and $NiH_2L$.[17] Bickley *et al.*,[18] performed a comprehensive Raman spectroscopic study of nickel(II) citrate and its aqueous solutions, and concluded that nickel(II) citrate existed as $Ni(Hcit)^-$ species in aqueous solution in confirmation of electrochemical studies on this system. In the present work, the complexation of different mol ratio of nickel to citrate was investigated in concentrated solution (≥1M) at pH 2–8, and several citrato nickel(II) complexes resulting from the reactions of nickel chloride or acetate and citrate were characterized. The X-ray crystal structures of $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2\cdot 2H_2O$, **1**, and $(NH_4)_4[Ni(Hcit)_2]\cdot 2H_2O$, **2** are reported.

## EXPERIMENTAL

### Synthesis of $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2\cdot 2H_2O$, 1

Complex **1** was prepared in a similar way to that reported for its potassium salt with some improvement.[15] An equimolar solution (2.0 M, 50 $cm^3$) of nickel chloride and ammonium citrate was reacted at room temperature overnight. The resulting mixture was placed in a refrigerator. After 2–3 days, green, platy crystals were obtained with a yield of 70%. *Anal.* Calcd. for $C_{12}H_{30}O_{20}N_2Ni_2$(%): C, 22.5; H, 4.7. Found: C, 22.1; H, 4.8. Electronic spectrum $\lambda_{max}$ (nm, ε, $M^{-1}$ $cm^{-1}$): 655 (2.4), 392 (5.9). IR bands observed using a Nicolet 740 (KBr disc): $\nu_{as}$(COO) $1599_{vs,w}$; $\nu_s$(COO) $1419_s$; $\nu_{as}$(Ni—O) $891_s$; $\nu_s$(Ni—O) $834_m$ $cm^{-1}$. In a similar procedure, green sodium and potassium salts, $Na_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O$, **3**, and $K_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O$, **4**, were obtained with IR bands (KBr disc): $\nu_{as}$(COO) $1625_s$, $1592_{vs}$, $1562_{vs}$; $\nu_s$(COO) $1415_s$, $1385_s$; $\nu_{as}$(Ni—O) $921_m$, $896_m$; $\nu_s$(Ni—O) $842_m$ $cm^{-1}$ for complex **3**, and $\nu_{as}$(COO) $1610_{vs}$, $1566_{vs}$; $\nu_s$(COO) $1410_{vs}$, $1386_s$; $\nu_{as}$(Ni—O) $916_m$, $885_s$; $\nu_s$(Ni—O) $831_m$ $cm^{-1}$ for complex **4**.

### Synthesis of $(NH_4)_4[Ni(Hcit)_2] \cdot 2H_2O$, 2

$NiCl_2 \cdot 6H_2O$ (0.02mol) added slowly with stirring to a solution of ammonium citrate $(NH_4)_3Hcit$ (1M, 40 $cm^3$). The resulting mixture was kept on a water bath at 85°C for two hours, then filtered and cooled. After 1–2 days, blue crystals of the complex were obtained with a yield of 60%. *Anal.* Calcd. for $C_{12}H_{30}O_{16}N_4Ni_1$(%): C, 26.4; H, 5.5. Found: C, 26.1; H, 5.3. Electronic spectrum $\lambda_{max}$ (nm, ε, $M^{-1} \cdot cm^{-1}$): 638 (2.0), 382 (4.3). IR bands (KBr disc): $\nu_{as}$(COO) $1605_s$, $1566_{vs}$; $\nu_s$(COO) $1400_s$; $\nu_{as}$(Ni—O) $905_m$; $\nu_s$(Ni—O) $847_m$ $cm^{-1}$.

### Transformation of $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O$, 1, and $(NH_4)_4[Ni(Hcit)_2] \cdot 2H_2O$, 2

To a solution of $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O$, **1** (1M, 10 $cm^3$), an equimolar amount of ammonium citrate was added. The mixture was kept on a water bath at 85 °C for two hours, then the solution was cooled slowly and placed in a refrigerator. After 1–2 days, blue crystals of **2** were obtained in 75% yield.

In another experiment, a solution of $(NH_4)_4[Ni(Hcit)_2] \cdot 2H_2O$, **2** (1M, 10 $cm^3$) was reacted with $NiCl_2 \cdot 6H_2O$ (0.01 mol) on a water bath at 85°C for two hours, and then the solution was cooled slowly and placed in a refrigerator. After 1–2 days, green crystals of **1** were obtained in 70% yield.

### X-ray data collection, structure solution and refinement

Crystals of suitable quality for X-ray diffraction were obtained as transparent green plates or blue prisms by slow evaporation of solutions of the title compounds at room temperature. The resulting crystals were sealed in capillaries to prevent loss of water molecules.

Crystallographic data for the two ammonium nickel citrates **1** and **2** are summarized in Table I. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated CuKα radiation at 296K. Lp factor, anisotropic decay and empirical absorption corrections were applied. The structures were solved by the heavy atom method and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all the non-hydrogen atoms. H atoms were located from difference maps. The hydrogen atoms were assigned appropriate isotropic temperature factors and included in structure factor calculations. All calculations were performed on a 586/100 microcomputer using the MoLEN software package. Positional parameters, selected atomic distances and bond angles are given in Tables II to V, respectively.

TABLE I Crystal data and summaries of intensity data collection and structure refinements

| *Compound* | $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O$,**1** | $(NH_4)_4[Ni(Hcit)_2] \cdot 2H_2O$,**2** |
|---|---|---|
| Colour/shape | green, plates | blue, prisms |
| Formula weight | 639.79 | 545.10 |
| Space group | $P\bar{1}$ | $P2_1/a$ |
| Temp., °C | 22 | 22 |
| Cell constants[a] | | |
| $a$, Å | 6.4071(7) | 9.361(1) |
| $b$, Å | 9.4710(7) | 13.496(1) |
| $c$, Å | 9.6904(5) | 9.4238(7) |
| α, deg | 105.064(5) | |
| β deg | 91.992(7) | 115.475(6) |
| γ, deg | 89.334(8) | |
| Cell volume, Å$^3$ | 567.5(1) | 1074.9(3) |
| Formula units/unit cell | 1 | 2 |
| $D_{calc}$, g cm$^{-3}$ | 1.872 | 1.684 |
| $\mu_{calc}$, cm$^{-1}$ | 29.502 | 20.732 |
| Diffractometer/scan | Enraf-Nonius CAD-4/2θ | Enraf-Nonius CAD-4/2θ |
| Radiation | CuKα (λ = 1.5418 Å) | CuKα (λ = 1.5418Å) |
| Max. crystal dimension, mm | 0.10 × 0.12 × 0.15 | 0.10 × 0.18 × 0.28 |
| Scan width | 0.55 + 0.35 tan θ | 0.65 + 0.35 tan θ |
| Standard reflections | 2 −3 −5; 2 6 1 | −6 −2 6; −5 −3 −2 |
| Decay of standards | 1.1% | −1.5% |
| Reflections measured | 2145 | 2134 |
| 2θ range, deg | $3 \leq \theta \leq 70$ | $3 \leq \theta \leq 70$ |
| Range of $h$, $k$, $l$ | 7, ±11, ±11 | −11, −16, ±11 |
| Reflections observed $I \geq 3\sigma(I)$[b] | 1714 | 1507 |
| Computer programs[c] | MoLEN | MoLEN |
| Structure solution | MoLEN | MoLEN |
| No. of parameters varied | 224 | 197 |
| Weights | unit weight | $[\sigma\|F_o\|^2 + 0.0004\|F_o\|^2+1]^{-1}$ |
| GOF | 0.791 | 0.831 |
| $R = \Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|$ | 0.037 | 0.052 |
| $R_w$ | 0.038 | 0.058 |
| Largest feature final diff. map | 0.46e$^-$ Å$^3$ | 0.81 e$^-$ Å$^3$ |

[a] Least-squares refinement of $[(\sin\theta)\lambda]^2$ values for 25 reflection θ>35° [b] Corrrections: Lorentz-polarization [c] Neutral scattering factors and anomalous corrections.

TABLE II Atomic coordinates and thermal parameters for $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O$

| *Atom* | *x/a* | *y/b* | *z/c* | $B_{eq}$ (Å$^2$)* |
|---|---|---|---|---|
| Ni(1) | 0.94174(9) | 0.24197(6) | 0.21041(6) | 1.63(1) |
| N(1) | 0.7767(5) | 0.3691(3) | 0.6156(3) | 2.32(6) |
| O(1) | 1.2158(3) | 0.1247(2) | 0.1573(2) | 1.72(4) |
| O(2) | 0.8696(4) | 0.0637(2) | 0.2768(3) | 2.32(5) |
| O(3) | 1.0875(4) | 0.3332(2) | 0.4019(2) | 1.96(5) |
| O(4) | 1.3456(4) | 0.3668(3) | 0.5633(3) | 2.58(5) |
| O(5) | 1.1831(4) | −0.1401(2) | −0.0140(3) | 2.40(5) |
| O(6) | 1.3991(4) | −0.3143(3) | 0.0216(3) | 3.33(6) |
| O(7) | 1.0132(4) | −0.1347(2) | 0.3226(3) | 2.52(5) |
| C(1) | 1.2417(5) | 0.0384(3) | 0.2607(3) | 1.47(6) |
| C(2) | 1.0241(5) | −0.0168(3) | 0.2886(4) | 1.76(6) |
| C(3) | 1.3384(5) | 0.1367(3) | 0.3978(4) | 1.83(6) |
| C(4) | 1.2505(5) | 0.2883(3) | 0.4571(4) | 1.66(6) |
| C(5) | 1.3914(5) | −0.0876(3) | 0.2006(4) | 1.80(6) |
| C(6) | 1.3206(5) | −0.1907(4) | 0.0608(4) | 2.05(7) |
| O(w1) | 0.6698(4) | 0.3566(3) | 0.2724(3) | 2.40(5) |
| O(w2) | 1.0455(4) | 0.4159(2) | 0.1385(3) | 2.21(5) |
| O(w3) | 1.2110(4) | 0.3544(3) | −0.1219(3) | 2.55(5) |

* $B_{eq} = 1/3\Sigma_i\Sigma_j B_{ij}a_ia_j$.

TABLE III Atomic coordinates and thermal parameters for $(NH_4)_4[Ni(Hcit)_2] \cdot 2H_2O$

| *Atom* | *x/a* | *y/b* | *z/c* | $B_{eq}$ (Å$^2$)* |
|---|---|---|---|---|
| Ni(1) | 1.000 | 0.000 | 1.000 | 2.16(2) |
| N(1) | 1.0724(5) | 0.2741(3) | 0.9093(4) | 3.60(9) |
| N(2) | 0.7391(4) | 0.0230(4) | 1.2389(4) | 3.75(9) |
| O(1) | 0.8776(3) | −0.1127(2) | 0.8592(3) | 2.27(6) |
| O(2) | 0.7738(3) | 0.0407(2) | 0.9502(3) | 2.51(6) |
| O(3) | 0.9819(3) | 0.0769(2) | 0.8026(3) | 2.79(6) |
| O(4) | 0.8852(5) | 0.1197(3) | 0.5531(4) | 6.8(1) |
| O(5) | 0.5508(5) | −0.1660(3) | 0.8798(4) | 6.25(9) |
| O(6) | 0.5413(5) | −0.2974(3) | 0.7454(4) | 7.2(1) |
| O(7) | 0.5424(3) | 0.0431(3) | 0.7396(3) | 3.37(7) |
| C(1) | 0.7370(4) | −0.0707(3) | 0.7371(4) | 2.23(8) |
| C(2) | 0.6778(4) | 0.0090(3) | 0.8161(4) | 2.32(8) |
| C(3) | 0.7733(5) | −0.0220(3) | 0.6098(4) | 2.41(8) |
| C(4) | 0.8879(5) | 0.0644(4) | 0.6593(4) | 2.95(9) |
| C(5) | 0.6147(5) | −0.1526(3) | 0.6608(4) | 2.58(9) |
| C(6) | 0.5632(5) | −0.2072(3) | 0.7708(4) | 2.54(9) |
| O(w1) | 0.8041(4) | −0.1991(3) | 1.3378(4) | 5.3(1) |

* $B_{eq} = 1/3\Sigma_i\Sigma_j B_{ij}a_ia_j$.

TABLE IV Selected bond lengths (Å) and angles (°) for $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni(1)—O(1) | 2.074(2) | Ni(1)—O(2) | 2.020(3) | Ni(1)—O(3) | 2.031(2) | Ni(1)—O(5a) | 2.037(2) |
| Ni(1)—O(w1) | 2.065(2) | Ni(1)—O(w) | 2.072(3) | O(1)—C(1) | 1.452(4) | O(2)—C(2) | 1.262(4) |
| O(3)—C(4) | 1.276(5) | O(4)—C(4) | 1.245(4) | O(5)—C(6) | 1.287(4) | O(6)—C(6) | 1.239(5) |
| O(7)—C(2) | 1.248(4) | C(1)—C(2) | 1.551(5) | C(1)—C(3) | 1.526(4) | C(1)—C(5) | 1.528(4) |
| C(3)—C(4) | 1.512(4) | C(5)—C(6) | 1.508(4) | O(1)—H(1) | 1.00(4) | | |

TABLE IV *(Continued)*

| | | | | | |
|---|---|---|---|---|---|
| O(1)—Ni(1)—O(2) | 81.53(9) | O(1)—Ni(1)—O(3) | 86.12(9) | O(1)—Ni(1)—O(5a) | 89.19(9) |
| O(1)—Ni(1)—O(w1) | 177.4(2) | O(1)—Ni(1)—O(w2) | 92.74(9) | O(2)—Ni(1)—O(3) | 90.6(1) |
| O(2)—Ni(1)—O(5a) | 88.5(2) | O(2)—Ni(1)—O(w1) | 96.7(2) | O(2)—Ni(1)—O(w2) | 174.2(1) |
| O(3)—Ni(1)—O(5a) | 175.30(9) | O(3)—Ni(1)—O(w1) | 92.0(1) | O(3)—Ni(1)—O(w2) | 88.4(1) |
| O(5a)—Ni(1)—O(w1) | 92.69(9) | O(5a)—Ni(1)—O(w2) | 92.1(1) | O(w1)—Ni(1)—O(w2) | 89.0(2) |
| Ni(1)—O(1)—C(1) | 105.1(2) | Ni(1)—O(2)—C(2) | 114.2(2) | Ni(1)—O(3)—C(4) | 128.3(2) |
| Ni(1)—O(5)—C(6) | 127.7(2) | C(1)—O(1)—H(1) | 102(3) | | |

Environment of $NH_4^+$ ion

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(1)· · ·O(3) | 2.877(4) | N(1)· · ·O(4b) | 2.790(4) | N(1)· · ·O(7c) | 2.768(4) | N(1)·· ·O(w2d) | 2.910(3) |

Hydrogen bonds

| | Dist. | O—H · · ·O | | Dist. | O—H · · ·O |
|---|---|---|---|---|---|
| O(1)· · ·O(5) | 2.629(3) | 145(4) | O(w1)· · ·O(4d) | 2.691(3) | 164(4) |
| O(w1)· · ·O(6e) | 2.792(4) | 155(4) | O(w2)· · ·O(w3) | 2.691(4) | 174(4) |
| O(w2)· · ·O(w3f) | 2.746(3) | 165(5) | | | |

Symmetry transformations *a*, (2–*x*, –*y*, 2–*z*); *b*, (–1+*x*, *y*, *z*); *c*, (2–*x*, –*y*, 1–*z*); *d*, (2–*x*, 1–*y*, 1–*z*); *e*, (2–*x*, –*y*, –*z*); *f*, (2–*x*, 1–*y*, –*z*).

TABLE V Selected bond lengths (Å) and angles(°) for $(NH_4)_4[Ni(Hcit)_2]\cdot 2H_2O$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni(1)—O(1) | 2.021(3) | Ni(1)—O(2) | 2.038(3) | Ni(1)—O(3) | 2.072(3) | O(1)—C(1) | 1.441(4) |
| O(2)—C(2) | 1.269(4) | O(3)—C(4) | 1.267(5) | O(4)—C(4) | 1.240(6) | O(5)—C(6) | 1.217(6) |
| O(6)—C(6) | 1.240(6) | O(7)—C(2) | 1.247(4) | C(1)—C(2) | 1.540(6) | C(1)—C(3) | 1.530(6) |
| C(1)—C(5) | 1.530(6) | C(3)—C(4) | 1.516(6) | C(5)—C(6) | 1.510(7) | O(1)—H(1) | 0.93(6) |

| | | | | | |
|---|---|---|---|---|---|
| O(1)—Ni(1)—O(1a) | 180.01(7) | O(1)—Ni(1)—O(2) | 79.2(1) | O(1)—Ni(1)—O(2a) | 100.8(1) |
| O(1)—Ni(1)—O(3) | 89.0(2) | O(1)—Ni(1)—O(3a) | 91.0(2) | O(2)—Ni(1)—O(2a) | 180.01(4) |
| O(2)—Ni(1)—O(3) | 89.0(1) | O(2)—Ni(1)—O(3a) | 91.1(1) | O(3)—Ni(1)—O(3a) | 180.01(3) |
| Ni(1)—O(1)—C(1) | 107.1(2) | Ni(1)—O(2)—C(2) | 111.1(3) | Ni(1)—O(3)—C(4) | 129.9(4) |
| C(1)—O(1)—H(1) | 111(3) | | | | |

Environment of $NH_4^+$ ion

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(1)· · ·O(1a) | 2.973(5) | N(1)· · ·O(3) | 2.843(5) | N(1)· : ·O(5b) | 2.811(7) | N(1)· · ·O(7c) | 2.887(5) |
| N(2)· · ·O(2) | 2.885(5) | N(2)· · ·O(3a) | 3.110(5) | N(2)· · ·O(4d) | 2.976(5) | N(2)· · ·O(7e) | 2.871(5) |

Hydrogen bonds

| | Dist. | O—H· · ·O | | Dist. | O—H· · ·O |
|---|---|---|---|---|---|
| O(1)· · ·O(6f) | 2.526(6) | 177(5) | O(wl)· · ·O(4a) | 2.845(6) | 154(5) |

Symmetry transformations *a*,(2–*x*, –*y*, 2–*z*;); *b*, (3/2–*x*, 1/2+*y*, 2–z); *c*,( –1/2+*x*, –1/2–*y*, *z*); *d*,(*x*, *y*, 1+*z*); *e*, (1–*x*, –*y*, 2–*z*); *f*,( –1/2+*x*, –3/2–*y*, *z*).

## RESULTS AND DISCUSSION

Preparation of the title compounds depends on pH control and the mol ratio of the reactants. Hedwig[16] reported a potentiometric and visible spectrophotometric study of the nickel(II)-citric acid system $(H^+)_p(Ni^{2+})_q(cit^{4-})_r$ in the pH range 3–6.

The dominant species is (1,1,1) for pH > 5 at 1:1 nickel/citrate. This is consistent with the preparation of sodium, potassium or ammonium dimeric nickel(II) citrate complexes in concentrated solution. The preparation of **1** was suggested *via* the following reaction.

$$2NiCl_2 + 2\ (NH_4)_3Hcit + 2H_2O \longrightarrow (NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot {}_2H_2O + {}_4NH_4Cl \quad (1)$$

Moreover, the preparation of dicitratonickelate(II) can be fulfilled *via* the following reaction.

$$NiCl_2 + 2\ (NH_4)_3Hcit + 2H_2O \longrightarrow (NH_4)_4[Ni(Hcit)_2]_2 \cdot 2H_2O + 2NH_4Cl \quad (2)$$

Transformations between **1** and **2** can be accomplished by the reaction with ammonium citrate or nickel chloride.

$$\begin{gathered}(NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O + 2(NH_4)_3Hcit \longrightarrow 2(NH_4)_4[Ni(Hcit)_2]_2 \cdot 2H_2O \\ NiCl_2(NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O + NH_4Cl\end{gathered} \quad (3)$$

Attempts to protonate **1** and **2** below pH 3 were unsuccessful, and led to decomposition of the complexes. This kind of reaction provide a good explantion for the removal and recovery of nickel ion in sodium citrate solution with a chelating resin containing a triethylenetetramine side chain.[19]

In the electronic spectra of both nickel citrates, shifts to higher frequencies of the two bands in dicitratonickelate(II), **2** (638, 382 nm), compared to those of **1** (655, 392 nm) are the result of the much stronger ligand field of the citrato ligand; there is also a marked shift compared to the $Ni^{2+}$ ion (720, 394 nm) consistent with the spectrochemical series of ligands.[11,17,20] Table VI shows comparisons of IR bands of the complexes. It can be seen that no IR band between 1740-1700cm$^{-1}$ is observed, indicateing that there is no associated carboxylic group. Typical of the spectra of **3** and **4** and dicitratonickelate(II), **2**, are well-resolved strong bands between 1625 and 1566 cm$^{-1}$, assignable to $\nu_{as}$(COO) and $\nu_s$(COO) bands between 1419 and 1385 cm$^{-1}$. They are all shifted with regard to citric acid or sodium citrate[21] and are not as well resolved in **1**,implying coodination of carboxylato groups, as confirmed by X-ray structural analyses.

TABLE VI Relevent infrared data ($cm^{-1}$) for the complexes

| *citric acid* | *sodium citrate* | ***1*** | ***2*** | ***3*** | ***4*** | *assignt.* |
|---|---|---|---|---|---|---|
| $3495_{vs}$,$3448_{w}$<br>$3298_{s,br}$ | | $3487_{vs}$ | $3550_{vs}$ | $3437_{vs}$ | $3511_{vs}$,$3447_{vs}$ | ν(OH) |
| | | $3115_{s,br}$ | $3172_{s,br}$ | | | ν(NH) |
| $1750_{vs}$,<br>$1704_{vs}$ | $1603_{m}$,<br>$1587_{s}$ | $1599_{vs,w}$ | $1605_{vs}$,<br>$1566_{vs}$ | $1625_{s}$,$1592_{vs}$,<br>$1562_{vs}$ | $1610_{vs}$,$1566_{vs}$ | $\nu_{as}$(COO) |
| $1430_{s}$,$1390_{s}$<br>$1359_{s}$ | $1439_{s}$,<br>$1418_{w}$ | $1419_{s}$, | $1400_{vs}$ | $1415_{s}$,$1385_{s}$ | $1410_{vs}$,$1386_{s}$ | $\nu_{s}$(COO) |
| | | $891_{s}$ | $905_{m}$ | $921_{m}$,$896_{m}$ | $916_{m}$,$885_{s}$ | $\nu_{as}$(NiO) |
| | | $834_{m}$ | $847_{m}$ | $842_{m}$ | $831_{m}$ | $\nu_{s}$(NiO) |

The complex $(NH_4)_2[Ni(Hcit)(H_2O)_2]_2 \cdot 2H_2O$, **1** exists as centrosymmetric dimers, as does its potassium salt[15], in which each citrate ion acts as a tetradentate ligand with the hydroxy, α-carboxyl and β-carboxyl oxygens coordinated to one nickel atom, and the other β-carboxylato group to a second nickel atom via a bridging bond (forming an intramolecular hydrogen bond [O(1)—H(1)· · ·O(5), 2.629(3)Å]). Octahedral coordination about the nickel atom is completed by the coordination of two water molecules. Figure 1 shows a perspective view of the dimeric anion.

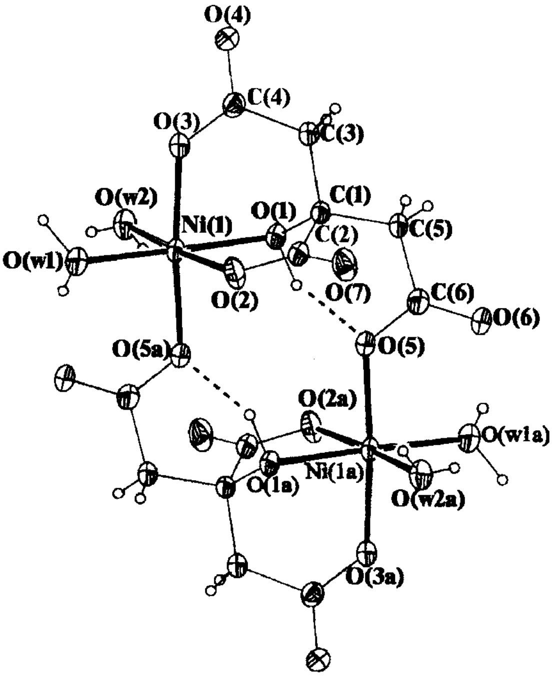

FIGURE 1 Perspective view of the anionic dimer $[Ni(Hcit)(H_2O)_2]_2^{2-}$ of **1**.

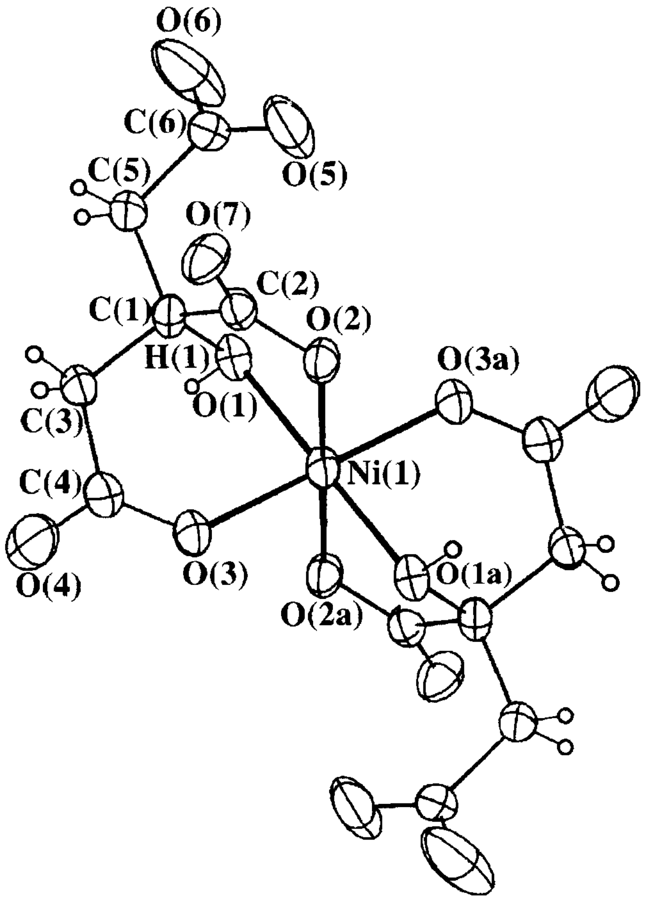

FIGURE 2 Perspective view of the anion $[Ni(Hcit)_2]^{4-}$ of **2**.

The crystal structure of $(NH_4)_4[Ni(Hcit)_2] \cdot 2H_2O$ **2** comprises discrete ammonium cations, water molecules and centrosymmetric dicitratonickelate anions. As shown in Figure 2, each citrate ion acts a as terdentate ligand coordinated to the same nickel atom *via* its hydroxyl, α- and β-carboxyl groups, while the other β-carboxyl group remains uncomplexed. The free β-carboxyl group is bonded with the hydroxy group of the other dicitrato nickel anion through a strong linear hydrogen bond [O(1)—H(1)· · ·O(6f), 2.526(6)Å].

Terdentate or tetradentate coordination of citrate through its hydroxyl, α-carboxyl and β-carboxyl group is a basic feature of mono- or dimeric nickel complexes. The structure of the Ni(II) complex of $cit^{4-}$, where bridging is through the ionized hydroxyl oxygens and carboxyl groups at higher pH, is polymeric.[5] Thus, the pH of the solution and the ratio of reactants are crucial factors for the formation of these species. It is undoubted that the hydroxyl group of the citrate ion carries a proton in the structure of **1** and **2**, since they were clearly visible in difference maps. The angle O(1)—Ni(1)—O(2) is 81.53(9)° for **1** and 79.2(1)° for **2**, reflecting the small distortion of the five-membered chelate ring formed by the hydroxyl oxygen and α-carboxyl group. The Ni—O(α-carboxyl) bond lies between 2.020(3) and 2.038(3) Å, for complex **2** and the Ni—O (hydroxyl) bond (2.021(3)Å) is shorter than that of Ni—O(β-carboxyl) bonds (2.072(3)Å), whereas for **1** and its potassium salt,[15] the Ni—O(hydroxyl) bond [2.074(2) or 2.125(3)Å] is much longer than the Ni—O(β-carboxyl) bonds [2.031(2), 2.037(2), 2.036, 2.075(3)Å]; this indicates the effects of different intramolecular and intermolecular hydrogen bonding.

## SUPPLEMENTARY MATERIAL

Complete lists of thermal parameters, bond distances, bond angles, hydrogen positions and observed and calculated structure factors for **1** (10 pages) **2** (9 pages) are available from the authors upon request.

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