Chelation of Nickel(II) by Citrate. The Crystal Structure of a Nickel–Citrate Complex, K₂[Ni(C₆H₅O₇)(H₂O)₂]₂·4H₂O

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Received November 26, 1982

The structure of a nickel-citrate complex, K₂[Ni-(C₆H₅O₇)(H₂O)₂]₂·4H₂O, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallises in the triclinic space group $P\bar{1}$, with Z = 1 and cell dimensions a = 6.729(1), b = 9.100(4), c = 10.594(2)Å, α = 94.86(2), β = 100.76(2), γ = 103.70(2)°. The structure was refined to a conventional R factor of 0.033 for 1804 reflections with $I > 2\sigma(I)$. The complex exists as centrosymmetric dimers, with each triionised citrate ion bound as a tridentate ligand (through two carboxylate oxygens and a hydroxyl oxygen) to one nickel atom, and providing a bridging bond to the second nickel atom through a third carboxylate oxygen. Octahedral coordination of the nickel atoms is completed by water molecules. Bond distances are Ni–O (carboxyl) 2.036(3), 2.054(3) and 2.075(3)Å, Ni–O (hydroxyl) 2.125(3)Å, and Ni–OH₂ 2.075(3) and 2.092(3)Å. The crystal structure is characterised by a network of interactions involving potassium ions, water molecules and nickel–citrate dimers.

Introduction

Citric acid (H₃Cit) is of widespread importance in biological systems and has a number of key physiological functions. Some of these depend on the chelating ability of citrate anions. Above pH 5.8 the triionised Cit³⁻ is the predominant form, but at high pH (*e.g.* > 11) it is possible to remove the proton from the hydroxyl group to give a tetraionised species. When citrate is bound to metal ions, the pH at which this proton is removed depends on the particular metal — for Cu(II) the tetraionised species is apparently formed at pH 4[1], while for Ni(II) it is not formed below pH 8–9 [2].

Previous structural studies on metal–citrate complexes have emphasized their enzymatic implications (for a review see [3]), particularly in relation to the enzyme aconitase [4–6]. Much attention has also focussed on the possible importance of citrate as a zinc-binding ligand in milk [7]. Our interest arose through the existence of nickel-accumulating plants, whose uptake of nickel apparently depends on chelation by anions of organic acids such as citric, malic

and malonic [8, 9]. In particular, in a number of New Caledonian species which act as hyperaccumulators of nickel, anionic nickel–citrate complexes are important [9].

Potentiometric and spectroscopic studies have characterised a variety of nickel(II)–citrate complexes [2, 10]. The only reported crystal structure analysis of a nickel–citrate complex is that of a complex of formula {[N(CH₃)₄]₅[Ni₄(C₆H₄O₇)₃(OH)(H₂O)]·18H₂O}₂, at pH 9.2, under which conditions the citrate ion is tetraionised [6]. Comparison with the structure we report here, of formulation K₂[Ni-(C₆H₅O₇)(H₂O)₂]₂·4H₂O, crystallised at pH 5 (near to the physiological pH for the nickel-accumulating plants), emphasizes the variation in complexation which can accompany variation in pH.

Experimental

Preparation and Characterisation

The complex was prepared by adding 150 ml of KOH solution (1.0 mol l⁻¹), slowly, with stirring, to 50 ml of 1.0 mol l⁻¹ citric acid solution, followed by the addition of 50 ml of a 1.0 mol l⁻¹ solution of NiCl₂·6H₂O. The pH was adjusted to 5.0 with further KOH if necessary. After 4–7 days green crystals of the complex were obtained. These had a reflectance spectrum essentially identical to that of the 1:1 nickel–citrate complex in dilute solution, with maxima at 393 nm and 670 nm. Microanalyses gave K 10.7, Ni 15.7, C 19.1, H 3.7, O 50.8%. Calculated values for KNiC₆H₅O₇·4H₂O are K 10.9, Ni 16.4, C 20.1, H 3.7, O 49.0%.

Crystallography

Preliminary unit cell dimensions were determined from oscillation, Weissenberg and precession photographs, and more accurate values from the least squares analysis of the positions of 25 general reflections on a four-circle X-ray diffractometer.

Crystal data

K₂[Ni(C₆H₅O₇)(H₂O)₂]₂·4H₂O, M = 717.6, Triclinic, a = 6.729(1), b = 9.100(4), c = 10.594(2) Å, $α$ = 94.86(2), $β$ = 100.76(2), $γ$ = 103.70(2)°, U =

613.5 Å^3, F(000) = 368 electrons, D_m = 1.93 g cm^{-3} (by flotation), Z = 1, D_c = 1.942 g cm^{-3}, Mo-Kα radiation, λ = 0.7107 Å, μ (Mo-Kα) = 10.1 cm^{-1}, space group P$\bar{1}$.

Data collection and reduction

Data were collected on an Enraf -Nonius CAD-4 diffractometer from a crystal of approximate dimensions 0.09 ×0.20 ×0.15 mm. The orientation of the crystal was defined by a least squares treatment of the positions of 25 general reflections. Data were collected in the $\omega-2\theta$ mode with a scan width $\Delta\omega$ = 0.70 + 0.35 tanθ. Three standard reflections, monitored after every 75 measurements, showed no systematic intensity changes. Reflections hkl, h̄kl, hk̄l and h̄k̄l were measured, for the range $1 < \theta < 27°$. Of the 2705 independent reflections measured, 1804 had intensities $I_{hkl} > 2\sigma(I_{hkl})$. Lorentz and polarisation corrections were applied to the data, but no correction was made for absorption.

Structure solution and refinement

The nickel atom positions were determined from a Patterson vector map, and the potassium ion, the citrate moiety and two coordinated water molecules were located from a subsequent heavy atom-phased electron density map. Three cycles of full-matrix least squares refinement, with isotropic thermal parameters, reduced the residual R to 0.148, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. The quantity minimised was $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = 4F_o^2/[\sigma(F_o)^2]^2$. The program used was CUCLS, a local version of ORFLS, adapted for the Burroughs B6700 compouter by the University of Canterbury. The inclusion of two more water molecules, following a difference electron density map, reduced R to 0.068, and after two more

cycles in which all atoms were given anisotropic thermal parameters, R was 0.042. All hydrogen atoms, including those of the water molecules, were clearly visible in a difference electron density map, and after their inclusion (although they were not refined) refinement converged at R = 0.033. No significant features remained unexplained in the difference map. Final atomic coordinates are listed in Table I.

Results and Discussion

The nickel–citrate complex forms centrosymmetric dimers in the crystal (see Fig. 1). Each citrate ion acts as a tridentate ligand to one nickel atom, coordinated through its hydroxyl group and two carboxylate groups, while its third carboxylate group is coordinated to the other nickel atom of the dimer. The octahedral coordination sphere of each nickel atom is completed by two bound water molecules. The potassium ions and the waters of crystallisation occupy the spaces between the nickel–citrate dimers.

Citrate coordination through the hydroxyl group, the central carboxylate group and one end carboxylate group confirms expectations from solution studies [10], and the structures of other metal–citrate complexes [3]. The citrate bridging seen here is similar to that observed in other metal complexes of triionised citrate ions (the isomorphous Mg(II), Mn(II) and Fe(II) complexes [4–6]) where the neighbouring nickel centres are bridged by carboxylate groups. A difference here, however, is that discrete dimers are formed, rather than chains of molecules. The structures contrast with the Cu(II) and Ni(II) complexes of tetraionised citrate, where bridg-

TABLE I. Fractional Atomic Coordinates.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ni	0.5145(1)	0.4959(1)	0.2485(1)	O(8)	0.5787(4)	0.2952(3)	0.1780(3)
K	0.3923(1)	0.8181(1)	0.0998(1)	O(9)	0.2781(4)	0.4904(3)	0.0951(3)
O(1)	0.7175(4)	0.6104(3)	0.1512(3)	O(10)	0.4562(5)	0.0604(4)	0.3115(3)
O(2)	0.9970(4)	0.7736(4)	0.1214(3)	O(11)	0.2217(5)	0.9965(4)	0.9205(4)
O(3)	0.9898(4)	0.6928(4)	0.7877(3)	C(1)	0.8969(6)	0.7052(5)	0.1947(4)
O(4)	0.6843(4)	0.6135(3)	0.6446(3)	C(2)	0.9941(6)	0.7342(5)	0.3383(4)
O(5)	0.5026(4)	0.7019(3)	0.3352(3)	C(3)	0.8522(6)	0.6956(4)	0.4344(4)
O(6)	0.7140(5)	0.9136(3)	0.4563(3)	C(4)	0.9841(6)	0.7412(5)	0.5707(4)
O(7)	0.7586(4)	0.5318(3)	0.4105(3)	C(5)	0.8805(6)	0.6786(5)	0.6767(4)
				C(6)	0.6736(6)	0.7777(5)	0.4084(4)
H(2a)	1.0606	0.8407	0.3531	H(9a)	0.1714	0.4212	0.1088
H(2b)	1.1049	0.6750	0.3553	H(9b)	0.2700	0.4550	0.0050
H(4a)	1.0139	0.8519	0.5953	H(10a)	0.3766	0.0716	0.3726
H(4b)	1.1120	0.6953	0.5700	H(10b)	0.5106	−0.0190	0.3454
H(7)	0.6973	0.5225	0.4857	H(11a)	0.1360	1.0655	0.9100
H(8a)	0.5455	0.2000	0.2000	H(11b)	0.1350	0.8980	0.8730
H(8b)	0.7250	0.3000	0.1900				
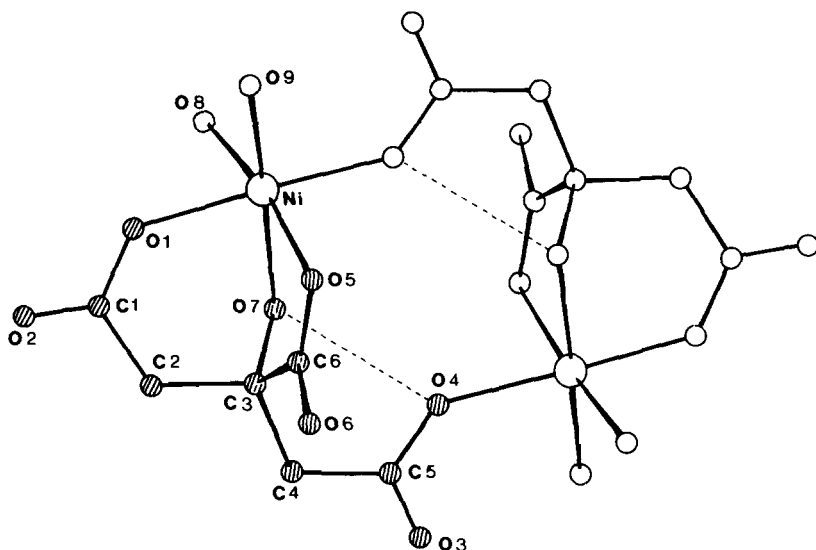
Fig. 1. A perspective diagram of the nickel–citrate dimer, $[Ni(C_6H_5O_7)(H_2O)_2]_2^{2-}$. Only non-hydrogen atoms are shown, and one citrate moiety is identified by cross-hatching. The numbering scheme corresponds to that of Glusker [3]. The intramolecular hydrogen bond between O(7) and O(4) is shown with a dotted line.

ing occurs through the ionised hydroxyl oxygens as well as carboxylate groups, leading to very complex polymeric structures [1, 6]. This could be a general difference between triionised and tetraionised citrate complexes, emphasising the importance of pH in determining the species formed.

There is no doubt that the hydroxyl group of the citrate ion carries a proton, since it was clearly visible in difference maps. An intracitrate hydrogen bond is formed, the proton H(7) being directed towards the bridging carboxylate oxygen, O(4) (see Table II). An exactly analogous intramolecular hydrogen bond occurs in the structure of the Mn(II)–citrate complex [5]. Bond lengths and angles in the citrate ion are generally as expected. The angles C(3)–C(2)–C(1) and C(3)–C(4)–C(5) (120.4(3) and 117.3(3)° respectively) are both greater than normal tetrahedral values (109.5°), but such an expansion, at the β-carbon atoms of the $-CH_2COO^-$ groups, is also observed in other metal–citrate complexes. Two of the carboxylate groups show significantly longer C–O bonds for the coordinated oxygen atom, but in the third (bridging) carboxylate the two C–O bond lengths are equal within experimental error.

Coordination about the nickel atom is distorted octahedral, with only one of the O–Ni–O angles deviating appreciably from regular octahedral values. The angle O(5)–Ni–O(7) is 78.5(1)°, reflecting the small bite of the five-membered chelate ring provided by the hydroxyl oxygen and the central carboxyl group. Similar values, 75–85°, are found in other metal citrates [1, 4, 6]. The Ni–O (carboxyl) bonds

(2.036(3), 2.054(3) and 2.075(3) Å, average 2.055 Å) are slightly shorter than the Ni–O (water) bonds (2.075(3) and 2.092(3) Å, average 2.083 Å), which are in turn shorter than the Ni–O (hydroxyl) bond (2.125(3) Å). In complexes where the hydroxyl oxygen is protonated the latter bond is also long, but where the hydroxyl group is ionised [1, 6] the bonds involving it are comparable with the metal–O (carboxyl) bonds.

The water molecules in the structure are involved in a comprehensive network of hydrogen bonds and interactions with either nickel or potassium (see Table II and Fig. 2). Thus O(8) and O(9) each form two hydrogen bonds and are coordinated to both nickel and potassium, O(10) is involved in three hydrogen bonds and is coordinated to potassium, and O(11) forms two hydrogen bonds and is coordinated to two potassium ions. Similarly the citrate carboxylate oxygens which are not coordinated to nickel are either hydrogen bonded to water or interact with the potassium ions. The hydrogen bond lengths (2.74–2.99 Å, average 2.83 Å) are normal, and the linearity of the hydrogen bonds is shown by the angles O–H ⋯ O (148–179°, average 163°).

The potassium ion is eight-coordinate. Six of the bonds, four to water molecules and two to citrate carboxylate oxygens, are in the range 2.653(3) to 2.956(3) Å (average 2.850 Å), comparable with K–O distances in other potassium salts (see for example [11, 12]). The other two bonds, to two further citrate carboxylate oxygens, are longer, at 3.186(3) and 3.218(3) Å. The geometry is that of a distorted

TABLE II. Bond Lengths (A) and Angles (degrees).

(a) *Nickel–citrate moiety*

Ni–O(1)	2.036(3)	C(2)–C(3)	1.556(5)
Ni–O(5)	2.054(3)	C(3)–O(7)	1.454(4)
Ni–O(7)	2.125(3)	C(3)–C(4)	1.554(5)
Ni–O(8)	2.092(3)	C(3)–C(6)	1.555(5)
Ni–O(9)	2.075(3)	C(4)–C(5)	1.544(5)
Ni–O(4^I)	2.075(3)	C(5)–O(3)	1.277(5)
C(1)–O(1)	1.285(5)	C(5)–O(4)	1.280(5)
C(1)–O(2)	1.254(5)	C(6)–O(5)	1.276(5)
C(1)–C(2)	1.561(6)	C(6)–O(6)	1.248(5)
O(1)–Ni–O(5)	89.0(1)	O(1)–C(1)–O(2)	120.1(4)
O(1)–Ni–O(7)	90.9(1)	O(1)–C(1)–C(2)	120.5(4)
O(1)–Ni–O(8)	87.6(1)	O(2)–C(1)–C(2)	119.4(4)
O(1)–Ni–O(9)	86.9(1)	C(1)–C(2)–C(3)	120.4(3)
O(1)–Ni–O(4^I)	177.2(1)	C(2)–C(3)–O(7)	107.0(3)
O(5)–Ni–O(7)	78.5(1)	C(2)–C(3)–C(4)	110.5(3)
O(5)–Ni–O(8)	170.3(1)	C(2)–C(3)–C(6)	108.4(3)
O(5)–Ni–O(9)	94.4(1)	C(4)–C(3)–O(7)	110.1(3)
O(5)–Ni–O(4^I)	89.0(1)	C(4)–C(3)–C(6)	112.4(3)
O(7)–Ni–O(8)	92.4(1)	C(6)–C(3)–O(7)	108.2(3)
O(7)–Ni–O(9)	172.6(1)	C(3)–C(4)–C(5)	117.3(3)
O(7)–Ni–O(4^I)	86.8(1)	C(4)–C(5)–O(3)	120.2(3)
O(8)–Ni–O(9)	94.5(1)	C(4)–C(5)–O(4)	115.7(4)
O(8)–Ni–O(4^I)	94.1(1)	O(3)–C(5)–O(4)	124.2(4)
O(9)–Ni–O(4^I)	95.2(1)	C(3)–C(6)–O(5)	116.9(3)
C(1)–O(1)–Ni	128.2(3)	C(3)–C(6)–O(6)	117.0(4)
C(6)–O(5)–Ni	114.6(2)	O(5)–C(6)–O(6)	126.0(4)
C(7)–O(7)–Ni	105.7(2)	Ni–O(4^I)–C(5^I)	129.1(3)

(b) *Hydrogen atoms*

O–H bonds range from 0.88 to 1.00 A, averaging 0.95 A.
C–H bonds range from 0.95 to 1.04 A, averaging 1.00 A.
Bond angles involving hydrogen atoms have approximately tetrahedral values, ranging from 93.4 to 128.1° (average 107.7°).

(c) *Environment of K$^+$ ion*

K–O(2^{II})	2.653(3)	K–O(11^{IV})	2.801(3)
K–O(5)	2.904(3)	K–O(11^V)	2.897(3)
K–O(9)	2.891(3)	K–O(1)	3.218(3)
K–O(10^{III})	2.956(4)	K–O(8^{VI})	3.186(3)

Bond angles around the K$^+$ ion have been deposited, with the thermal parameters and structure factors.

(d) *Hydrogen bonds*

	Dist.	O–Ĥ ⋯ O		Dist.	O–Ĥ ⋯ O
O(7) ⋯⋯ O(4)	2.78	148	O(10) ⋯⋯ O(6^{VIII})	2.78	151
O(8) ⋯⋯ O(10)	2.75	152	O(10) ⋯⋯ O(6^I)	2.99	162
O(8) ⋯⋯ O(3^{VII})	2.83	179	O(11) ⋯⋯ O(2^{IV})	2.85	170
O(9) ⋯⋯ O(3^I)	2.74	154	O(11) ⋯⋯ O(3^{II})	2.93	173
O(9) ⋯⋯ O(1^{VI})	2.78	174			

Roman numerals denote symmetry-related positions

I	1–x, 1–y, 1–z		V	x, y, –1 + z
II	–1 + x, y, z		VI	1–x, 1–y, –z
III	x, 1 + y, z		VII	2–x, 1–y, 1–z
IV	1–x, 2–y, 1–z		VIII	x, –1 + y, z

square antiprism, with the two square faces made up of O(5), O(10), O(11), O(1) and O(2), O(11), O(8), O(9).

Titrimetric studies [10] of acidic and neutral solutions containing nickel and citrate, both at con-centrations below 0.01 mol l^{-1}, showed no evidence of the formation of the dimeric species [NiCit]$_2^{2-}$. Further investigation is warranted, to see if this species exists in concentrated solutions as well as in the solid state.
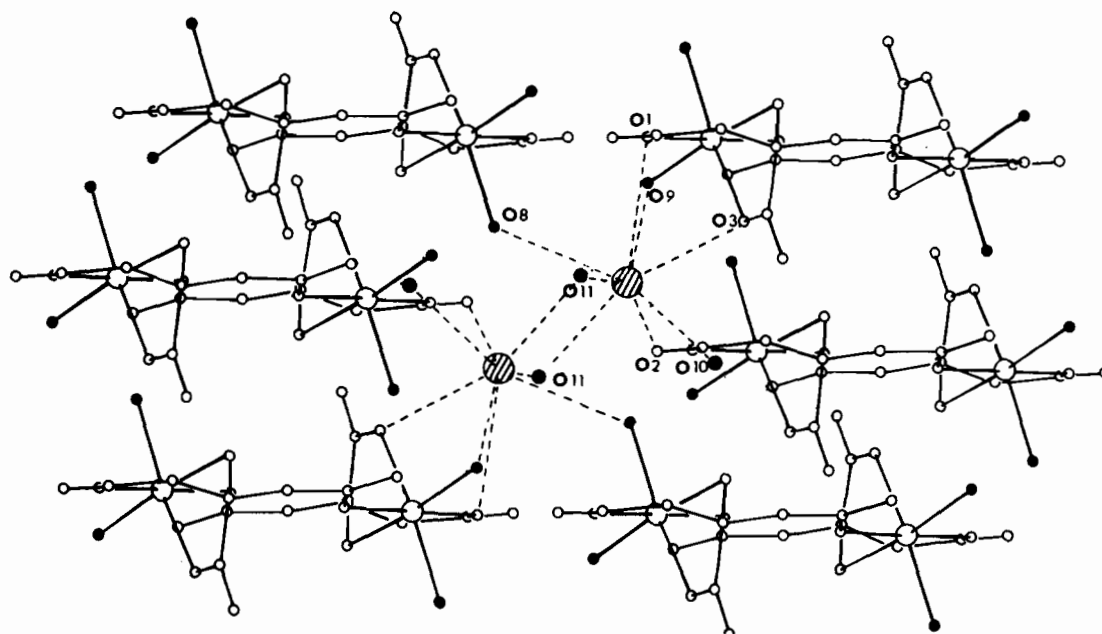
Fig. 2. A diagram showing the environment of the potassium ions (cross-hatched) and water molecules (filled circles) in the spaces between nickel–citrate dimers. For clarity only two potassium ions are shown, their interactions with neighbouring oxygen atoms being shown by broken lines.

In the light of the clear evidence for the existence of 2:1 citrate:nickel complexes in near-neutral aqueous solutions containing excess citrate [10], it will also be of interest to attempt to prepare solids containing the $[NiCit_2]^{4-}$ anion, and to determine their crystal structures.

Acknowledgements

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