

Structure of Trisodium Bis(nitrilotriacetato)ferrate(III) Pentahydrate, Na₃[Fe{N(CH₂CO₂)₃}₂].5H₂O

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Abstract. $M_r = 591.1$, monoclinic, $P2_1/n$, $a = 10.102$ (1), $b = 10.859$ (1), $c = 20.441$ (2) Å, $\beta = 102.78$ (1)°, $V = 2186.8$ Å³, $Z = 4$, $D_x = 1.795$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.83$ mm⁻¹, $F(000) = 1212$, $T = 291$ K, $R = 0.042$ for 3402 observed reflections. The Fe atom has distorted pentagonal bipyramidal coordination with two axial O, three equatorial O and two equatorial N atoms. One nitrilotriacetate ligand is tetradentate, the other tridentate with one carboxylate group uncoordinated. The water molecules are not coordinated to Fe.

Introduction. The 'complexone' family of multidentate chelating ligands, such as ethylenediaminetetraacetate (edta), tends to form seven-coordinate complexes with Fe^{III} as is shown by reported crystal structures (Lind, Hamor, Hamor & Hoard, 1964; Cohen & Hoard, 1966; Novozhilova, Polynova & Porai-Koshits, 1975; Nesterova, Polynova & Porai-Koshits, 1975; Chuklanova, Polynova, Poznyak, Dikareva & Porai-Koshits, 1981; Solans, Font Altaba & Garcia-Orcaín, 1984). Such complexes may be useful as model compounds for the metal binding sites in nucleotides (Rabinowitz, Davis & Herber, 1966). Nitrilotriacetic acid [H₃nta = *N,N*-bis(carboxymethyl)glycine], a member of the complexone family, can act in its deprotonated form as a tetradentate ligand, as observed in Cu and Co complexes of nta (Whitlow, 1973; Battaglia, Corradi & Tani, 1975).

Four compounds of Fe^{III} with nta ligands have been reported. Brintzinger & Hesse (1942) synthesized compounds with metal–ligand ratios of 1:1 and 2:3. Krishnamurthy, Morris & Hambright (1970) report a compound with a 1:2 ratio, and Krishnamurthy & Morris (1972) report a 1:3 compound. No crystallographic investigations have been performed on these substances, probably owing to the difficulty in obtaining suitable single crystals. We have prepared a new, highly crystalline Fe^{III}–nta complex, Na₃[Fe(nta)₂].5H₂O, and determined its crystal structure.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å² $\times 10^4$)

	x	y	z	U
Fe	2667 (1)	2178 (1)	3881 (1)	180 (1)
N(1)	412 (3)	1738 (2)	3777 (1)	177 (8)
C(11)	-319 (3)	2363 (3)	3161 (2)	258 (11)
C(12)	560 (3)	2333 (3)	2641 (2)	228 (10)
O(11)	1826 (2)	2218 (2)	2871 (1)	247 (7)
O(12)	14 (3)	2433 (3)	2042 (1)	392 (9)
C(13)	6 (3)	2187 (3)	4386 (2)	258 (11)
C(14)	1186 (3)	2032 (3)	4979 (2)	230 (10)
O(13)	2354 (2)	2060 (2)	4845 (1)	303 (8)
O(14)	992 (3)	1917 (2)	5555 (1)	326 (8)
C(15)	302 (3)	384 (3)	3718 (2)	271 (11)
C(16)	1613 (3)	-275 (3)	3693 (2)	224 (10)
O(15)	2695 (2)	342 (2)	3764 (1)	294 (8)
O(16)	1557 (2)	-1402 (2)	3599 (1)	332 (9)
N(2)	4255 (3)	3292 (2)	3467 (1)	183 (8)
C(21)	3532 (3)	4393 (3)	3156 (2)	213 (10)
C(22)	2516 (3)	4802 (3)	3558 (2)	232 (10)
O(21)	2152 (2)	3984 (2)	3946 (1)	261 (7)
O(22)	2088 (3)	5866 (2)	3506 (1)	344 (9)
C(23)	5295 (3)	3626 (3)	4074 (2)	277 (11)
C(24)	5475 (3)	2592 (4)	4577 (2)	329 (12)
O(23)	4567 (2)	1757 (2)	4469 (1)	308 (8)
O(24)	6458 (3)	2621 (3)	5061 (1)	668 (12)
C(25)	4830 (3)	2546 (3)	2995 (2)	212 (10)
C(26)	5901 (3)	3162 (3)	2671 (2)	216 (10)
O(25)	6297 (2)	2523 (2)	2236 (1)	281 (8)
O(26)	6318 (2)	4210 (2)	2861 (1)	334 (8)
Na(1)	1304 (1)	2708 (2)	1221 (1)	402 (5)
Na(2)	4822 (1)	1874 (1)	1214 (1)	270 (4)
Na(3)	2992 (2)	1659 (2)	6481 (1)	441 (5)
O(3)	4460 (3)	787 (3)	5821 (1)	427 (10)
O(4)	3527 (3)	693 (3)	97 (1)	377 (9)
O(5)	8124 (3)	5038 (3)	2173 (1)	531 (12)
O(6)	8429 (4)	5413 (4)	3852 (2)	802 (15)
O(7)	-851 (7)	1455 (6)	696 (3)	1646 (35)

$U = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$

Table 2. Bond lengths (Å) and angles (°) for the Fe coordination

Fe–N(1)	2.291 (3)	Fe–O(11)	2.053 (2)
Fe–O(13)	2.067 (2)	Fe–O(15)	2.010 (2)
Fe–N(2)	2.314 (3)	Fe–O(21)	2.040 (2)
Fe–O(23)	2.078 (2)		
N(1)–Fe–O(11)	74.3 (1)	N(1)–Fe–O(13)	73.5 (1)
O(11)–Fe–O(13)	147.5 (1)	N(1)–Fe–O(15)	79.7 (1)
O(11)–Fe–O(15)	85.1 (1)	O(13)–Fe–O(15)	93.5 (1)
N(1)–Fe–N(2)	146.2 (1)	O(11)–Fe–N(2)	77.7 (1)
O(13)–Fe–N(2)	130.2 (1)	O(15)–Fe–N(2)	116.5 (1)
N(1)–Fe–O(21)	86.8 (1)	O(11)–Fe–O(21)	89.4 (1)
O(13)–Fe–O(21)	84.5 (1)	O(15)–Fe–O(21)	166.4 (1)
N(2)–Fe–O(21)	74.3 (1)	N(1)–Fe–O(23)	141.3 (1)
O(11)–Fe–O(23)	135.2 (1)	O(13)–Fe–O(23)	75.6 (1)
O(15)–Fe–O(23)	79.3 (1)	N(2)–Fe–O(23)	72.5 (1)
O(21)–Fe–O(23)	113.0 (1)		

Experimental. The complex was prepared by addition of 30 mmol NaOH and subsequently 5 ml 1M aqueous FeCl₃ to a suspension of 10 mmol H₃nta in 12 ml water. Addition of excess acetone gave a dark-brown sticky tar, recrystallized by cooling from an ethanol–water solution.

Yellow crystal, 0.21 × 0.46 × 0.58 mm, mounted on glass fibre. Stoe–Siemens AED diffractometer, unit-cell parameters refined from 2θ values of 32 reflections centred at ±ω (20 < 2θ < 25°). 3840 unique reflections with 2θ < 50°, h 0→12, k 0→12, l -24→24, on-line profile-fitting (Clegg, 1981), no significant intensity variation for three standard reflections, semi-empirical absorption corrections based on ellipsoid model and 386 azimuthal scan data for sets of equivalent reflections, transmission 0.62 to 0.67, 3402 reflections with $F > 4\sigma(F)$. Multisolution direct methods, blocked-cascade refinement on F , $w^{-1} = \sigma^2(F) + 0.00039F^2$ automatically optimized, H atoms constrained to give C–H = 0.96 Å, O–H = 0.87 Å, H–C–H = H–O–H = 109.5° (no H atoms for one H₂O with high thermal motion), $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.2U_{\text{eq}}(\text{O})$, anisotropic thermal parameters for non-H atoms, no extinction correction, scattering factors from *International Tables for X-ray Crystallography* (1974). 328 parameters, $R = 0.042$, $wR = 0.058$, slope of normal probability plot = 1.51, max. $\Delta/\sigma = 0.036$, mean = 0.009, largest peak in final difference map = 0.71 e Å⁻³, largest hole = -0.74 e Å⁻³. Programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2.* Fig. 1 shows the structure of the anion.

The Fe atom is seven-coordinate with a N₂O₅ donor set. The approximate coordination geometry is that of a pentagonal bipyramid, as is observed in most [Fe(edta)-(H₂O)]⁻ complexes: two O atoms from different nta ligands occupy the axial positions, while three O and two N atoms make up the equatorial belt. There is considerable distortion from an ideal pentagonal bipyramidal geometry, as a result of the restricted ‘bite’ of the N–C–C–O sections of the ligands: N–Fe–O angles in the five chelate rings lie in the range 73.5 (1)–79.7 (1)°. Thus, angles subtended at Fe by neighbouring equatorial atoms are reasonably close to the ideal value of 72° for a pentagonal bipyramid [72.5 (1)–77.7 (1)°], but there are large deviations of

equatorial–Fe–axial angles from 90°, and the inter-axial angle itself is reduced from 180 to 166.4 (1)°.

One of the nta ligands is tetradentate, but the other is only tridentate, one of the carboxylate groups remaining uninvolved in the metal coordination. Tridentate Hnta occurs in the structure of Ba[Mo₃O₃S(Hnta)₃].10H₂O (Shibahara, Hattori & Kuroya, 1984), but in this case the ligand is singly protonated; in the [Fe(nta)₂]³⁻ anion, all three carboxylate functional groups of both of the ligands are deprotonated. The two Fe–N bond lengths [mean 2.30 (1) Å] are considerably greater than the Fe–O bond lengths [mean 2.05 (3) Å]. Despite this, both N atoms are coordinated to Fe at the expense of one potential Fe–carboxylate linkage. Although water usually completes the seven-coordinate of Fe in complexes of the hexadentate edta (Cohen & Hoard, 1966; Nesterova *et al.*, 1975; Novozhilova *et al.*, 1975; Lind *et al.*, 1964; Solans *et al.*, 1984), and is also coordinated to Co in K[Co(nta)(H₂O)].2H₂O (Battaglia *et al.*, 1975), it plays no direct part in the Fe coordination in Na₃[Fe(nta)₂].5H₂O. The water molecules form hydrogen bonds with each other and with carboxylate O atoms, and participate in coordination of the Na⁺ ions.

Each Na⁺ ion lies within 3 Å of six O atoms (two or three water molecules and four or three carboxylate O atoms uncoordinated to Fe), giving irregular coordination geometries: Na–O distances range from 2.310 (3) to 2.698 (3) Å with one other at 2.993 (4) Å, and O–Na–O angles range from 64.6 (2) to 176.0 (1)°.

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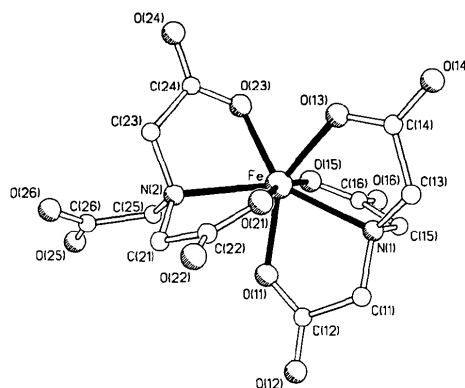


Fig. 1. Structure of the [Fe(nta)₂]³⁻ anion, projected approximately on the equatorial plane, showing the atom-numbering scheme. H atoms are omitted.

* Tables of structure factors, anisotropic thermal parameters, H-atom parameters, other bond lengths and angles, and hydrogen-bond distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39674 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Calcium Chloride–Sarcosine (1/3), $\text{CaCl}_2 \cdot 3\text{C}_3\text{H}_7\text{NO}_2$, in the Ferroelectric Phase

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Abstract. $M_r = 378.3$, orthorhombic, $Pn2_1a$, $a = 9.122$ (4), $b = 17.408$ (4), $c = 10.228$ (8) Å, $V = 1624$ (2) Å³, $Z = 4$, $D_x = 1.55$ Mg m⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.729$ mm⁻¹, $F(000) = 792$, $T = 118$ (1) K, ferroelectric structure, $R = 0.036$ for 5951 unique reflections. The molecule is deformed slightly from the reported paraelectric structure. Short atomic distances are seen for Ca–O bonds. Major positional differences between the two phases are found in O atoms and CH₃ groups, which also exhibit relatively large thermal vibrations.

Introduction. Tris-sarcosine calcium chloride (TSCC), $\text{CaCl}_2 \cdot 3(\text{CH}_3\text{NH}_2^+\text{CH}_2\text{COO}^-)$, undergoes a ferroelectric phase transition at about $T_c = 127$ K (Pepinsky & Makita, 1962). Dielectric and thermal properties (Makita, 1965; López-Echarri & Tello, 1981) suggest that the phase transition is of the order–disorder type. Indeed, dielectric critical slowing down was observed in the GHz region around T_c (Deguchi, Aramaki, Nakamura & Tanaka, 1983). On the other hand, the soft phonon modes were found in the far-IR region by spectroscopic studies (Prokhorova, Smolensky, Siny, Kuzminov, Mikvabia & Arndt, 1980; Chen, Schaack & Winterfeldt, 1981; Kozlov, Volkov, Scott & Feldkamp, 1983). To reconcile this with the controversy about the

transition mechanism, Chen & Schaack (1984) proposed a pseudospin–phonon coupled model. In order to clarify the mechanism of the phase transition, it is necessary to determine the crystal structures of TSCC both above and below the phase-transition temperature. The paraelectric structure at room temperature has already been reported (Ashida, Bando & Kakudo, 1972). Hence, we determined the ferroelectric structure at 118 K as part of a continuing study of the mechanism of the phase transition from the structural point of view.

Experimental. Single crystals grown by slow cooling of aqueous solution at about 320 K. Spherical specimen, diameter 0.40 mm. Rigaku AFC-5 diffractometer with graphite monochromator. 25 reflections in range $17 < \theta < 22^\circ$ for measuring lattice parameters. ω – 2θ scan mode. 6848 independent reflections measured with $2\theta < 90^\circ$. 6378 observed [$|F_o| > \sigma(|F_o|)$]; 427 of these rejected because of the extinction effect and unbalanced backgrounds. Lorentz–polarization correction. No absorption correction ($\mu r = 0.15$). Systematic absences: $hk0$ for h odd, $0kl$ for $k + l$ odd. $Pn2_1a$ because of polar phase. Three standard reflections measured after every 200 reflections, intensity fluctuations within 5% during data collection. Anisotropic full-matrix least-squares