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A Mixed Cation Ternary Nitroprusside: $[(CH_3)_4N][Na][Fe(CN)_5(NO)].2.5H_2O$

John J. Longridge, Jeremy M. Rawson and John E. Davies

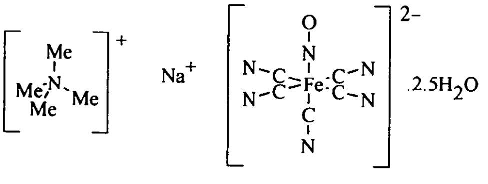
Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England. E-mail: jjl22@cus.cam.ac.uk

Abstract

The title compound, sodium tetramethylammonium pentacyano(nitrosyl)ferrate(II) 2.5-hydrate, is a ternary nitroprusside with an asymmetric unit composed of an octahedral nitroprusside anion, a disordered tetrahedral tetramethylammonium cation, a sodium cation and 2.5 water solvate molecules.

Comment

In the course of our work on nitroprusside salts (Longridge, Ludman, Rawson & Davies, 1996), while attempting the preparation of bis(tetramethylammonium) nitrosylpentacyanoferrate(II), we isolated the title compound, (I), in which the nitroprusside anion was associated with two different counterions, *i.e.* $[(CH_3)_4N]^+$ and Na^+.



(I)

In the nitroprusside anion, five cyanide ligands and one nitrosyl group form a distorted octahedral array about the Fe atom. The Fe—N distance [1.654 (4) Å] is considerably shorter than the Fe—C distance [mean 1.9354 (5) Å] and is in agreement with other determinations on nitroprusside salts (Castellano, Piro & Rivero, 1977; Mullica, Sappenfield, Tippin & Leschnitzer, 1989; Mullica, Tippin & Sappenfield, 1990). The tetramethylammonium counterion exhibits some disorder which has been modelled over two sites, with the site occupancies in the approximate ratio 1:2. The disorder closely approximates to rotation about one of the tetramethylammonium threefold axes. The sodium cation exhibits secondary bonding to the O atoms of three neighbouring water molecules [2.302 (4)–2.574 (4) Å] and to the N atoms of two neighbouring cyano groups [2.406 (4) and 2.474 (5) Å], forming an approximate trigonal bipyramidal arrangement. One of the water molecules (O2*W*) bridges to a symmetry-related sodium cation. The two N atoms of the cyanide groups take up one axial and one equatorial position about the sodium cation, and are themselves *trans* with respect to one another within the nitroprusside dianion. This combination of interactions leads to layers composed of nitroprusside anions and solvated Na^+ anions interspersed with layers of $[(CH_3)_4N]^+$ cations.

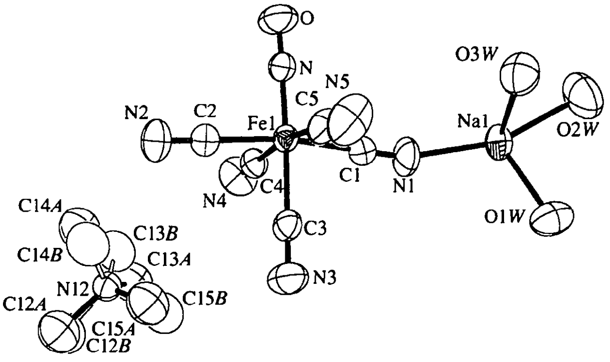


Fig. 1. The asymmetric unit of $[(CH_3)_4N][Na][Fe(CN)_5(NO)].2.5H_2O$ showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

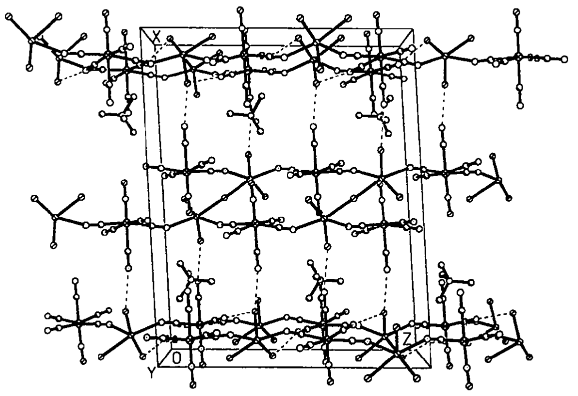


Fig. 2. Packing diagram viewed down the *y* axis.

Experimental

The synthesis of (I) was carried out by reaction of warm aqueous solutions of $Na_2Fe(CN)_5(NO).2H_2O$ and $(CH_3)_4NCl$ in a 1:2 molar ratio. Instead of the expected $[(CH_3)_4N]_2[Fe(CN)_5(NO)]$ product, crystals of $[(CH_3)_4N][Na][Fe(CN)_5(NO)].2.5H_2O$ were obtained by slow evaporation over 24 h at 273 K. A crystal suitable for X-ray diffraction was grown by evaporation of an aqueous solution over 1 h at room temperature.

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Crystal data

$(C_4H_{12}N)Na[Fe(CN)_5(NO)]$.-
$2.5H_2O$
$M_r = 358.14$
Monoclinic
$C2/c$
$a = 21.454\,(4)$ Å
$b = 9.107\,(2)$ Å
$c = 17.364\,(3)$ Å
$\beta = 93.57\,(3)°$
$V = 3386.0\,(11)$ Å^3
$Z = 8$
$D_x = 1.405$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 30$–$40°$
$\mu = 0.938$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.25 \times 0.10 \times 0.10$ mm
Orange

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: none
2837 measured reflections
2494 independent reflections
1961 observed reflections
$[I > 2\sigma(I)]$

$R_{\rm int} = 0.0250$
$\theta_{\rm max} = 24.99°$
$h = 0 \rightarrow 24$
$k = 0 \rightarrow 10$
$l = -20 \rightarrow 18$
3 standard reflections
monitored every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0477$
$wR(F^2) = 0.1259$
$S = 1.086$
2490 reflections
213 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 8.61P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.307$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.39$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Fe1	0.08062 (3)	0.02356 (6)	0.12291 (3)	0.0346 (2)
N	0.0049 (2)	0.0563 (4)	0.1251 (2)	0.0437 (9)
C1	0.0848 (2)	−0.1026 (5)	0.2128 (3)	0.0457 (11)
N3	0.2225 (2)	−0.0219 (6)	0.1221 (3)	0.0718 (13)
C2	0.0908 (2)	0.1425 (5)	0.0314 (3)	0.0434 (11)
C3	0.1697 (2)	−0.0054 (5)	0.1224 (2)	0.0454 (11)
O	−0.0461 (2)	0.0849 (5)	0.1282 (2)	0.0742 (11)
N2	0.0964 (2)	0.2106 (5)	−0.0223 (2)	0.0660 (12)
C4	0.1023 (2)	0.1883 (5)	0.1892 (3)	0.0460 (11)
C5	0.0739 (2)	−0.1511 (6)	0.0594 (3)	0.0549 (13)
N5	0.0707 (3)	−0.2559 (6)	0.0231 (3)	0.092 (2)
N1	0.0867 (2)	−0.1772 (5)	0.2657 (2)	0.0686 (13)
N4	0.1141 (2)	0.2838 (5)	0.2301 (3)	0.0758 (14)
N12	0.2434 (2)	0.5140 (4)	0.1166 (2)	0.0471 (9)
C12*A*†	0.2954 (10)	0.602 (3)	0.0829 (14)	0.098 (2)
C13*A*†	0.2386 (10)	0.547 (2)	0.1973 (8)	0.098 (2)
C14*A*†	0.1850 (8)	0.554 (2)	0.0701 (11)	0.098 (2)
C15*A*†	0.2579 (9)	0.3555 (17)	0.1003 (13)	0.098 (2)
C12*B*‡	0.2962 (6)	0.6092 (17)	0.0992 (8)	0.098 (2)
C13*B*‡	0.2050 (6)	0.5875 (13)	0.1771 (7)	0.098 (2)
C14*B*‡	0.2003 (5)	0.4885 (14)	0.0488 (6)	0.098 (2)
C15*B*‡	0.2677 (5)	0.3741 (12)	0.1496 (8)	0.098 (2)
Na1	0.06176 (9)	−0.3542 (2)	0.36185 (10)	0.0558 (5)
O1*W*	0.1429 (2)	−0.5188 (5)	0.3570 (3)	0.0810 (13)
O2*W*	0.0030 (3)	−0.5425 (7)	0.4142 (3)	0.128 (2)
O3*W*	0	−0.4850 (7)	0.25	0.086 (2)

† Site occupancy = 0.368 (10). ‡ Site occupancy = 0.632 (10).

Table 2. *Selected geometric parameters (Å, °)*

Fe1—N	1.654 (4)	N2—Na1$^{\rm i}$	2.474 (5)
Fe1—C3	1.929 (5)	C4—N4	1.142 (6)
Fe1—C4	1.930 (5)	C5—N5	1.144 (6)
Fe1—C5	1.935 (5)	N1—Na1	2.406 (4)
Fe1—C1	1.936 (5)	Na1—O1*W*	2.302 (4)
Fe1—C2	1.947 (5)	Na1—O2*W*	2.344 (5)
N—O	1.128 (5)	Na1—N2$^{\rm ii}$	2.474 (5)
C1—N1	1.140 (5)	Na1—O3*W*	2.574 (4)
N3—C3	1.144 (6)	O3*W*—Na1$^{\rm iii}$	2.574 (4)
C2—N2	1.133 (5)		
N—Fe1—C3	177.3 (2)	C1—Fe1—C2	170.6 (2)
N—Fe1—C4	92.7 (2)	O—N—Fe1	176.7 (4)
C3—Fe1—C4	84.7 (2)	O1*W*—Na1—O2*W*	87.9 (2)
N—Fe1—C5	97.0 (2)	O1*W*—Na1—N1	102.1 (2)
C3—Fe1—C5	85.6 (2)	O2*W*—Na1—N1	155.1 (2)
C4—Fe1—C5	170.1 (2)	O1*W*—Na1—N2$^{\rm ii}$	100.6 (2)
N—Fe1—C1	94.9 (2)	O2*W*—Na1—N2$^{\rm ii}$	102.3 (2)
C3—Fe1—C1	85.8 (2)	N1—Na1—N2$^{\rm ii}$	98.1 (2)
C4—Fe1—C1	89.0 (2)	O1*W*—Na1—O3*W*	91.5 (2)
C5—Fe1—C1	88.3 (2)	O2*W*—Na1—O3*W*	71.9 (2)
N—Fe1—C2	94.5 (2)	N1—Na1—O3*W*	85.0 (2)
C3—Fe1—C2	84.9 (2)	N2$^{\rm ii}$—Na1—O3*W*	166.50 (15)
C4—Fe1—C2	91.1 (2)	Na1—O3*W*—Na1$^{\rm iii}$	124.9 (3)
C5—Fe1—C2	90.0 (2)		

Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $x, -y, \frac{1}{2} + z$; (iii) $-x, y, \frac{1}{2} - z$.

The tetramethylammonium cation was found to be disordered. Two sets of C atoms were refined with equivalent displacement parameters and idealized tetrahedral geometries to give final site-occupancy factors of 0.632 (10) and 0.368 (10). Methyl H atoms were added at calculated positions using a riding model, with $U({\rm H}) = 1.5U_{\rm iso}({\rm C})$. H atoms associated with the water molecules were located in the difference map during subsequent cycles of least squares. Their positions were restrained with equivalent O—H distances and refined with a fixed displacement parameter of $U({\rm H}) = 0.08 \times 10^3$ Å^2.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1089). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexaaquacobalt(II) Bis(2-aminotoluene-4-sulfonate)

Brian J. Gunderman,[a] Surendra N. Dubey[b] and Philip J. Squattrito[a]*

[a]*Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, USA, and* [b]*Department of Chemistry, Kurukshetra University, Kurukshetra 132119, Haryana, India. E-mail: 3clwp5s@cmuvm.csv.cmich.edu*

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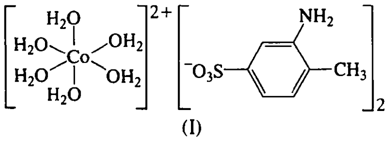
Abstract

The title compound, $[Co(H_2O)_6](C_7H_8NO_3S)_2$, has a structure built of segregated layers of hexaaquacobalt(II) cations and 2-aminotoluene-4-sulfonate anions. The Co atom is in a fairly regular octahedral coordination environment of water molecules [Co—O range 2.046 (3)–2.111 (3) Å]. The anions are arranged with the sulfonate groups directed to opposite faces of the layer in an alternating fashion. The layers are held together by a series of O—H···O hydrogen bonds between the water molecules and sulfonate O atoms [H···O range 1.89 (4)–2.10 (4) Å]. The Mn and Zn salts are isostructural. These features are similar to those of other divalent metal organosulfonate salts.

Comment

The title compound, (I), was prepared and characterized as part of a larger study (Shubnell, Kosnic & Squattrito, 1994) of the coordination behavior and structural trends of transition metal organosulfonate salts. Our studies (Kosnic, McClymont, Hodder & Squattrito, 1996) and others (Aquino, Clegg, Liu & Sykes, 1995; Couldwell, Prout, Robey, Taylor & Rossotti, 1978; Henderson & Nicholson, 1995) have shown that the first-row transition metal cations tend to crystallize as hexaaqua complexes in the presence of a variety of organosulfonate anions. The resulting structures have alternating layers of hexaaqua cations and organosulfonate anions. The anions are usually interleaved, having the sulfonate groups directed to both faces of the layer, though double layers are also sometimes observed. The layers are held together by hydrogen bonding between the coordinated water molecules and sulfonate O atoms. One sulfonate which does readily coordinate to transition metal cations is sulfanilate (4-aminobenzenesulfonate), which forms structures in which the anion layers are linked by direct bonding between the metal and both sulfonate O and amine N atoms (Shakeri & Haussuhl, 1992*a*; Gunderman, Squattrito & Dubey, 1996). Consequently, we were interested in the reactions of other amino-substituted benzenesulfonic acids and the possibility of obtaining structures similar to those of the sulfanilate salts.



(I)

The cobalt 2-aminotoluene-4-sulfonate salt has no direct bonding between the Co atom and the O or N atoms of the anion (Fig. 1). The cation rests on a center of inversion in a fairly regular octahedral environment of water molecules. Although there is some variation in the Co—O bond distances (Table 2), they are all within the reported range for $[Co(H_2O)_6]^{2+}$ complexes (Cotton, Daniels, Murillo & Quesada, 1993). The geometry of the sulfonate anion is as expected and similar to that of the parent acid (Shubnell & Squattrito, 1994). The extended structure of this salt (Fig. 2) has its essential features in common with the previously reported structures of non-coordinating sulfonates. The hexaaqua complexes form planar layers in between slabs of anions. The phenyl rings of the anions are approximately perpendicular to the plane of the layer. Alternating anions have the sulfonate group directed to the opposite face of the layer, with the long axes of the anions canted slightly in opposite directions. This packing affords the formation of a short almost linear O—H···$O_{sulfonate}$ hydrogen bond involving each water H atom (Table 3). The amine groups are somewhat in the interior of the layer and the H atoms have no short contacts (< 2.3 Å) with the O atoms. The Mn and Zn salts are isostructural with the Co salt on the basis of their unit-cell parameters [Mn: a = 7.095 (2), b = 6.301 (2), c = 24.715 (8) Å, β = 90.07 (2)°; Zn: a = 7.012 (2), b = 6.271 (2), c = 24.455 (5) Å, β = 90.17 (2)°] and Laue symmetry as determined in this laboratory.

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