

Pentasodium *trans*-Tetracyanodisulphitocobaltate(III) Tridecahydrate

BY MILJA ASPLUND, SUSAN JAGNER* AND EVERT LJUNGSTRÖM

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg,
S-412 96 Göteborg, Sweden

(Received 18 September 1981; accepted 26 November 1981)

Abstract. $\text{Na}_5[\text{trans-Co}(\text{CN})_4(\text{SO}_3)_2] \cdot 13\text{H}_2\text{O}$, $M_r = 672.3$, $P2_1/c$, $a = 8.893(1)$, $b = 16.893(4)$, $c = 16.258(5)$ Å, $\beta = 93.27(2)^\circ$ at 168 K, $Z = 4$, $D_c = 1.83$ Mg m $^{-3}$, $\mu(\text{Mo } K\alpha) = 1.08$ mm $^{-1}$. Least-squares refinement (4143 reflections, single-crystal X-ray diffractometer data collected at 168 K) gave $R = 0.047$ for 319 parameters. There are two independent complex ions, each with Co at a centre of symmetry. For ion (1), Co–S is 2.262(1) Å and S–O 1.486(3)–1.495(3) Å; for ion (2) Co–S is 2.279(1) Å and S–O 1.478(3)–1.498(3) Å. The Co–C and C–N distances lie in the range 1.877(4)–1.896(3) Å and 1.144(5)–1.159(5) Å, respectively.

Introduction. The structure of $\text{K}_5\text{Na}_5[\text{cis-Co}(\text{CN})_4(\text{SO}_3)_2]_2 \cdot 9\text{H}_2\text{O}$ has recently been reported (Jagner & Ljungström, 1982), in connection with studies on the mode of coordination of sulphite in the presence of cyanide. In order to investigate whether or not there exist structural differences between the $[\text{cis-Co}(\text{CN})_4(\text{SO}_3)_2]^{5-}$ ion and its *trans* counterpart, the crystal structure of $\text{Na}_5[\text{trans-Co}(\text{CN})_4(\text{SO}_3)_2] \cdot 13\text{H}_2\text{O}$ has now been determined.

The title compound was prepared by the method of Rây & Chackrabarty (1933) for $\text{Na}_5[\text{Co}(\text{CN})_4(\text{SO}_3)_2] \cdot 12\text{H}_2\text{O}$, modified according to Chen, Tsao, Gaver, Tewari & Wilmarth (1966). Recrystallization from a solution of Na_2SO_3 (0.75 mol dm $^{-3}$) and NaOH (0.5 mol dm $^{-3}$) yielded pale-yellow prismatic crystals of sodium *trans*-tetracyanodisulphitocobaltate(III), formulated as the tridecahydrate, $\text{Na}_5[\text{trans-Co}(\text{CN})_4(\text{SO}_3)_2] \cdot 13\text{H}_2\text{O}$, in accordance with the results of the structural analysis.

Weissenberg photographs showed the crystals to be monoclinic with $h0l$: $l = 2n + 1$ and $0k0$: $k = 2n + 1$ systematically absent, indicating space group $P2_1/c$. Intensities from a crystal, $0.19 \times 0.14 \times 0.16$ mm, were measured at 168 K with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo $K\alpha$ radiation and the ω - 2θ scan technique with a variable scan rate of 2–10° min $^{-1}$ in 2θ . A Syntex LT1 low-temperature device, which has a temperature stability of the order of

± 2 K, was used to maintain the temperature. Data were collected for $2\theta \leq 60^\circ$ with $h \geq 0$ and $k \geq 0$, 7803 reflections being measured. That the crystal was not subject to decay was verified by the periodic measurement of the intensities of two reflections. A 96-step profile was recorded for each reflection and the Lehmann & Larsen (1974) profile-analysis method was used to calculate the intensities (Lindqvist & Ljungström, 1979). Correction was made for Lorentz and polarization effects but not for absorption. Symmetry-related reflections were merged and systematically absent reflections excluded giving a unique set of 7145 reflections; of these, 4143 had $I > 3.0\sigma(I)$ and were considered to be observed. The unit-cell parameters at 168 K were determined by least squares from diffractometer setting angles for 15 reflections.

The structure was solved from Patterson and successive electron density maps. The Co atoms were found to occupy the special positions 2(a) and 2(d), there thus being two independent half-anions in the asymmetric unit. Block-diagonal least-squares refinement of the positional and anisotropic thermal parameters and a scale factor gave $R = 0.047$ for 4143 reflections and 319 parameters. For the 7145 data comprising both observed and unobserved reflections $R = 0.091$. The F_o values were weighted according to $w = (a + F_o + cF_o^2)^{-1}$ (Cruickshank, 1970) with $a = 32.0$ and $c = 0.010$. Scattering factors for the uncharged atoms were taken from Doyle & Turner (1968). Calculations were carried out on an IBM 360/65–370/145 computer system using programs described by Lindgren (1977); drawings were prepared with ORTEP (Johnson, 1965). A final difference map showed a maximum electron density of 1.0 e Å $^{-3}$. No attempt was made to locate the H atoms. Atomic coordinates are listed in Table 1.†

† Lists of structure factors, anisotropic thermal parameters, cation contacts, O...O and O...N contacts < 3 Å and a comparison of the O(–SO $_3$) environments in $\text{Na}_5[\text{trans-Co}(\text{CN})_4(\text{SO}_3)_2] \cdot 13\text{H}_2\text{O}$ and in $\text{K}_5\text{Na}_5[\text{cis-Co}(\text{CN})_4(\text{SO}_3)_2]_2 \cdot 9\text{H}_2\text{O}$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36578 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* To whom correspondence should be addressed.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å²)

$$B_{eq} = 8\pi^2/3 (U_{11}a^{*2}a^2 + \dots + U_{23}b^*c^*bc \cos \alpha)$$

where

$$T = \exp[-2\pi^2 (U_{11}h^2a^{*2} + \dots + U_{23}klb^*c^*)].$$

E.s.d.'s are given in parentheses. Aq denotes the oxygen atom of a water molecule.

	x	y	z	B _{eq}
Co(1)	0.0	0.0	0.0	0.65 (1)
S(1)	0.02127 (9)	0.12604 (5)	0.04616 (5)	0.90 (1)
O(11)	0.1718 (3)	0.1389 (2)	0.0890 (2)	1.62 (5)
O(12)	-0.0975 (3)	0.1452 (2)	0.1037 (2)	1.76 (5)
O(13)	0.0051 (3)	0.1826 (2)	-0.0245 (2)	1.66 (4)
C(11)	0.2042 (4)	0.0008 (2)	-0.0234 (2)	1.00 (5)
N(11)	0.3293 (4)	-0.0002 (2)	-0.0391 (2)	1.49 (5)
C(12)	0.0507 (4)	-0.0326 (2)	0.1093 (2)	1.32 (6)
N(12)	0.0835 (5)	-0.0518 (3)	0.1754 (2)	2.16 (6)
Co(2)	0.5	0.0	0.5	0.64 (1)
S(2)	0.47875 (9)	0.12405 (5)	0.44545 (5)	0.92 (1)
O(21)	0.3314 (3)	0.1336 (2)	0.3986 (2)	1.91 (5)
O(22)	0.6023 (3)	0.1438 (2)	0.3919 (2)	1.97 (5)
O(23)	0.4836 (4)	0.1831 (2)	0.5143 (2)	1.90 (5)
C(21)	0.7025 (4)	-0.0059 (2)	0.4734 (2)	1.17 (5)
N(21)	0.8257 (4)	-0.0094 (2)	0.4557 (2)	1.56 (5)
C(22)	0.4422 (4)	-0.0403 (2)	0.3940 (2)	1.13 (5)
N(22)	0.4068 (4)	-0.0648 (2)	0.3292 (2)	1.99 (6)
Na(1)	-0.0634 (2)	0.4234 (1)	0.0761 (1)	1.69 (3)
Na(2)	0.6278 (2)	0.1150 (1)	0.1353 (1)	1.99 (3)
Na(3)	-0.1400 (2)	0.1018 (1)	0.3561 (1)	1.70 (3)
Na(4)	0.5484 (2)	0.4257 (1)	0.4136 (1)	1.65 (3)
Na(5)	0.7671 (2)	0.3213 (1)	0.2396 (1)	2.29 (3)
Aq(1)	0.0998 (3)	0.0354 (2)	0.3334 (2)	1.72 (5)
Aq(2)	0.7146 (3)	0.3128 (2)	0.3874 (2)	1.98 (5)
Aq(3)	0.7753 (4)	0.3041 (2)	0.0932 (2)	2.16 (5)
Aq(4)	0.4018 (3)	0.0415 (2)	0.1715 (2)	1.99 (5)
Aq(5)	0.4659 (3)	0.1573 (3)	0.0202 (2)	1.87 (5)
Aq(6)	0.3013 (4)	0.2800 (2)	0.1467 (2)	2.02 (5)
Aq(7)	0.5656 (4)	0.2174 (2)	0.2307 (2)	2.17 (5)
Aq(8)	-0.0692 (3)	0.2064 (2)	0.2664 (2)	1.92 (5)
Aq(9)	0.3844 (4)	0.3942 (2)	0.2976 (2)	2.14 (5)
Aq(10)	0.1983 (4)	0.2761 (2)	0.3484 (2)	2.19 (5)
Aq(11)	0.0225 (3)	0.1554 (2)	0.4680 (2)	1.75 (5)
Aq(12)	0.0464 (4)	0.3640 (2)	0.1919 (2)	2.62 (6)
Aq(13)	0.2294 (4)	0.5376 (2)	0.2669 (2)	2.83 (6)

Discussion. Bond lengths and angles within the [*trans*-Co(CN)₄(SO₃)₂]⁵⁻ ion are given in Table 2 and views of the crystallographically independent complex ions are shown in Fig. 1. The unit cell is depicted in Fig. 2. Na₅[*trans*-Co(CN)₄(SO₃)₂].13H₂O contains Na⁺ ions, complex ions and water molecules in an almost C-centred arrangement, the pseudo-centring being seriously violated only by Aq(9) and Aq(12).

In both the complex ions the configuration of ligands about Co is distorted octahedral [approximately 2/m (C_{2h}) symmetry] with the sulphite groups *trans* and in the staggered conformation. This is in contrast to K₃Na₅[*cis*-Co(CN)₄(SO₃)₂].9H₂O (Jagner & Ljungström, 1982) in which the [*cis*-Co(CN)₄(SO₃)₂]⁵⁻ ion has approximately mm2 (C_{2v}) symmetry. The Co—S

Table 2. Bond lengths (Å) and angles (°) within the [Co(CN)₄(SO₃)₂]⁵⁻ ions

Ion (1)		Ion (2)	
Co(1)—S(1)	2.262 (1)	Co(2)—S(2)	2.279 (1)
Co(1)—C(11)	1.877 (4)	Co(2)—C(21)	1.879 (4)
Co(1)—C(12)	1.890 (3)	Co(2)—C(22)	1.896 (3)
S(1)—O(11)	1.489 (3)	S(2)—O(21)	1.486 (3)
S(1)—O(12)	1.486 (3)	S(2)—O(22)	1.478 (3)
S(1)—O(13)	1.495 (3)	S(2)—O(23)	1.498 (3)
C(11)—N(11)	1.156 (5)	C(21)—N(21)	1.150 (5)
C(12)—N(12)	1.144 (5)	C(22)—N(22)	1.159 (5)
Co(1)—C(11)—N(11)	178.4 (3)	Co(2)—C(21)—N(21)	178.8 (3)
Co(1)—C(12)—N(12)	179.0 (4)	Co(2)—C(22)—N(22)	180.0 (3)
Co(1)—S(1)—O(11)	110.4 (1)	Co(2)—S(2)—O(21)	110.5 (1)
Co(1)—S(1)—O(12)	111.4 (1)	Co(2)—S(2)—O(22)	112.9 (1)
Co(1)—S(1)—O(13)	110.1 (1)	Co(2)—S(2)—O(23)	108.9 (1)
O(11)—S(1)—O(12)	109.0 (2)	O(21)—S(2)—O(22)	109.7 (2)
O(11)—S(1)—O(13)	108.1 (2)	O(21)—S(2)—O(23)	107.3 (2)
O(12)—S(1)—O(13)	107.7 (2)	O(22)—S(2)—O(23)	107.4 (2)
S(1)—Co(1)—C(11)	89.8 (1)	S(2)—Co(2)—C(21)	91.1 (1)
S(1)—Co(1)—C(12)	87.2 (1)	S(2)—Co(2)—C(22)	88.0 (1)
C(11)—Co(1)—C(12)	90.6 (2)	C(21)—Co(2)—C(22)	89.2 (2)

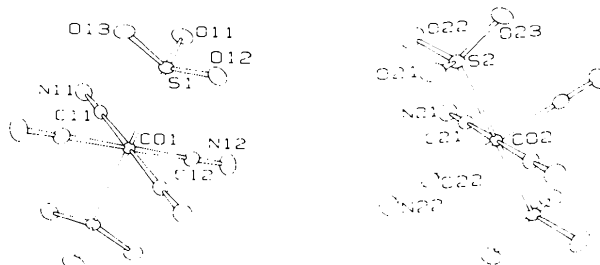
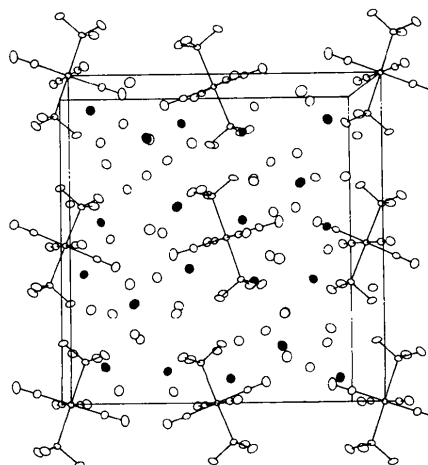


Fig. 1. The two crystallographically independent complex ions showing the atomic numbering.

Fig. 2. View of the structure down a*; Na⁺ ions filled, b is †, c —.

distances in the two [*trans*-Co(CN)₄(SO₃)₂]⁵⁻ ions differ [2.262 (1), 2.279 (1) Å], that of ion (2) being the longest reported hitherto for sulphitocobaltate(III) complexes (*cf.* Fallon, Raston, White & Yandell, 1980; Jagner & Ljungström, 1982). The close similarity

between Co—S in [*trans*-Co(CN)₄(SO₃)₂]⁵⁻ and Fe—S in [Fe(CN)₅SO₃]⁵⁻, 2.255 (1) and 2.277 (1) Å (Jagner, Ljungström & Tullberg, 1980), provides further evidence for an appreciable d_{π} - d_{π} contribution to the Fe—S bond in the latter ion, since Co^{III}—S would be expected to be of the order of 0.1 Å shorter than Fe^{II}—S were the metal-sulphur bonds of pure σ character in both ions. The Co—C and C—N distances do not differ between ion (1) and ion (2) and agree well with those found in K₅Na₅[*cis*-Co(CN)₄(SO₃)₂]₂.9H₂O (Jagner & Ljungström, 1982).

Apart from the staggered conformation of the sulphite ligands and the long Co(2)—S(2) bond, there are no marked differences between the *trans*-tetra-cyanodisulphitocobaltate(III) ion and its *cis* counterpart. There would, however, appear to be slight differences in the geometries of the sulphite ligands, e.g. a tendency towards longer intrasulphite O...O contacts in the *trans* complex {[*trans*-Co(CN)₄(SO₃)₂]⁵⁻: O...O = 2.407 (5)–2.423 (4) Å for ion (1) and 2.399 (5)–2.424 (4) Å for ion (2); [*cis*-Co(CN)₄(SO₃)₂]⁵⁻: 2.386 (5)–2.398 (5) Å for sulphite (1) and 2.364 (5)–2.369 (6) for sulphite (2)}. The S—O distances and O—S—O angles lie in the range 1.478 (3)–1.498 (3) Å and 107.3 (2)–109.7 (2)° for the *trans* and 1.462 (4)–1.483 (3) Å and 107.2 (2)–108.4 (2)° for the *cis* ion, respectively. The lengthening of S—O due to interactions with H- or O-containing species and small cations is well documented (e.g. Raston, White & Yandell, 1979; Larsson, 1971). A comparison* between O(—SO₃) contacts in Na₅[*trans*-Co(CN)₄(SO₃)₂].13H₂O and in K₅Na₅[*cis*-Co(CN)₄(SO₃)₂]₂.9H₂O shows no definite correlation between the length of a given S—O bond and the environment of the relevant O. Sulphite oxygen atoms in [*trans*-Co(CN)₄(SO₃)₂]⁵⁻ exhibit, however, on average a larger number of contacts to water molecules than is the case for [*cis*-Co(CN)₄(SO₃)₂]⁵⁻, where O(—SO₃) contacts are predominantly to cations.

It is conceivable that the disparity between Co—S distances in Na₅[*trans*-Co(CN)₄(SO₃)₂].13H₂O might be attributable to the slight differences in the O(—SO₃) environments* of the ligands in the two ions. A similar effect has been reported for Na₂ClO₄[*cis*-Co-

(C₂H₈N₂)₂(SO₃)₂].3H₂O (Raston, White & Yandell, 1979).

The four Na⁺ ions Na(1)–Na(4) all have six O or N neighbours in the range 2.301 (4)–2.587 (4) Å. Na(5) has four oxygen atoms of water molecules (Aq) and one N at 2.403 (4)–2.674 (4) Å and a further Aq and N at 2.741 (4) and 2.839 (5) Å, respectively. There are several close contacts* between water molecules and O- or N-containing species. A detailed description of the hydrogen-bonding network is not, however, feasible without knowledge of the positions of the H atoms.

The authors thank Professor N.-G. Vannerberg for valuable discussions. Financial support from the Swedish Natural Science Research Council (NFR, Contract No. 2286-101) is gratefully acknowledged.

* See deposition footnote.

References

- CHEN, H. H., TSAO, M.-S., GAVER, R. W., TEWARI, P. H. & WILMARTH, W. K. (1966). *Inorg. Chem.* **5**, 1913–1920.
- CRUICKSHANK, D. W. J. (1970). In *Crystallographic Computing*, p. 195. Copenhagen: Munksgaard.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- FALLON, G. D., RASTON, C. L., WHITE, A. H. & YANDELL, J. K. (1980). *Aust. J. Chem.* **33**, 665–670.
- JAGNER, S. & LJUNGSTRÖM, E. (1982). *Acta Cryst.* **B38**, 231–234.
- JAGNER, S., LJUNGSTRÖM, E. & TULLBERG, A. (1980). *Acta Cryst.* **B36**, 2213–2217.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LARSSON, L. O. (1971). *Chem. Commun. Univ. Stockholm*, No. V.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- LINDGREN, O. (1977). *An Integrated Set of Crystallographic Programs*. In *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates*. Thesis, Department of Inorganic Chemistry, Chalmers Univ. of Technology and Univ. of Göteborg, Göteborg, Sweden.
- LINDQVIST, O. & LJUNGSTRÖM, E. (1979). *J. Appl. Cryst.* **12**, 134.
- RASTON, C. L., WHITE, A. H. & YANDELL, J. K. (1979). *Aust. J. Chem.* **32**, 291–296.
- RÄY, P. R. & CHACKRABARTY, S. CH. (1933). *Z. Anorg. Allgem. Chem.* **221**, 173–184.

* See deposition footnote.