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Tris(1,10-phenanthroline)sodium 2,4,6-trimercapto-1,3,5-triazin-1-ide

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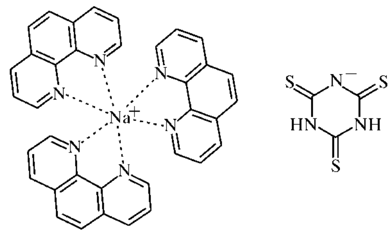
The title compound, $[Na(C_{12}H_8N_2)_3](C_3H_2N_3S_3)$, contains an Na^+ centre which is ionically bonded to three 1,10-phenanthroline (phen) ligands and one trithiocyanurate(1−) ($ttcH_2$) anion. In the crystal structure, the anions are linked *via* hydrogen bonds to form linear chains. The S and H atoms of the $ttcH_2$ anion participate in intermolecular $N-H\cdots S$ hydrogen bonding, with $N\cdots S$ distances of 3.298 (2) and 3.336 (2) Å. The phen ligands are almost parallel, with dihedral angles of 3.92 (5), 11.75 (5) and 15.45 (5)°; moreover, they are nearly perpendicular to the $ttcH_2$ chains, with angles of 81.94 (7), 85.86 (7) and 85.96 (7)°.

Comment

Trithiocyanuric acid (2,4,6-trimercaptotriazine, $ttcH_3$) and its trisodium salt are very important compounds because they are used for the precipitation of many heavy metals from waste water (Henke *et al.*, 2000; Matlock *et al.*, 2001, 2002). Moreover, the resulting precipitates can be subsequently converted, by increasing the pH of the solution, to useful sulfides and non-toxic cyanuric acid (Bailey *et al.*, 2001). Trithiocyanuric acid also shows antitoxoplasmal activity and is more effective than 5-fluorouracil and emimicin (Iltzsch & Tankersley, 1994). An important factor in the synthesis of compounds with $ttcH_3$ is the pH value (Krepps *et al.*, 2001; Cecconi *et al.*, 2003; Mahon *et al.*, 2003). Moreover, up to six atoms of $ttcH_3$ can be used for coordination to metal centres. Thus, miscellaneous types of compounds can be synthesized, which can be mononuclear as well as polynuclear, with the trithiocyanurate anion acting as a bridge. Some structures of complexes of the trithiocyanurate anion with group I and II metals have been published recently, *e.g.* with Li^I (Clegg *et al.*, 1998; Armstrong *et al.*, 2000), Na^I and K^I (Cecconi *et al.*, 2003; Mahon *et al.*, 2003), and Ca^{II}, Sr^{II}, Ba^{II} and Mg^{II} (Henke & Atwood, 1998; Henke *et al.*, 2001). The title compound, (I), was prepared as a by-product during our efforts to synthesize an Mg^{II} complex with $ttcH_3$ and 1,10-phenanthroline (phen).



(I)

Compound (I) consists of $[Na(phen)_3]^+$ and $[ttcH_2]^-$ moieties. The Na^I ion is six-coordinated by the N atoms of the three phen ligands. The Na—N distances vary from 2.430 (2) to 2.656 (3) Å and compare well with the average length of 2.54 Å for Na—N distances in related compounds contained in the Cambridge Structural Database (Version 5.24.1; Allen, 2002). All the phen ligands are nearly coplanar (the average and maximum deviations of contributing atoms from the least-squares planes are 0.04 and 0.08 Å, respectively) and almost parallel. The angles between phen *A* (atoms N1–C14) and phen *B* (atoms N15–C28), phen *A* and phen *C* (atoms N29–C42), and phen *B* and phen *C* are 11.75 (5), 3.92 (5) and 15.45 (5)°, respectively. The average intermolecular distance between phen ligands (*A*–*B*, *A*–*C*, *B*–*C*) in the $[Na(phen)_3]^+$ units is 3.5 Å [symmetry codes: $(x+\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z)$ for *A*–*B*; $(x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z)$ for *A*–*C*].

The six-membered ring of the $[ttcH_2]^-$ anion is also almost planar; the average and maximum deviations of contributing atoms from the least-squares planes are 0.04 and 0.06 Å, respectively. The Cremer–Pople puckering parameters (Cremer & Pople, 1975) for the ring are $Q = 0.102$ (2) Å, $\theta = 93(1)°$ and $\varphi_2 = -27(1)°$. Atoms S1 and S2 are significantly

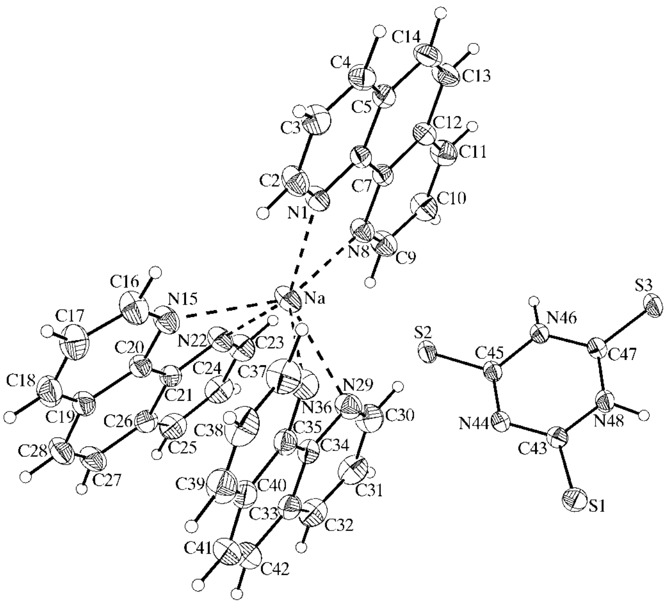


Figure 1
The molecular structure of (I) (*ORTEP*III; Johnson & Burnett, 1996), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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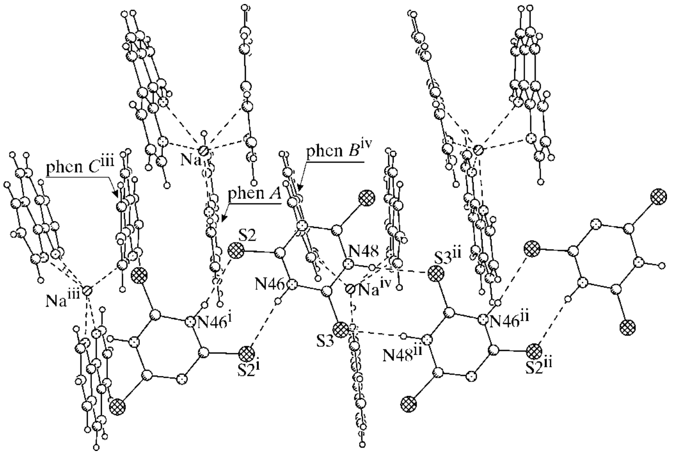

Figure 2
Part of the crystal structure of (I), showing the formation of a chain of $[ttcH_2]^-$ and $[Na(phen)_3]^+$ moieties [symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, -y, 1 - z$; (iii) $x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$].

shifted from the mean plane through the ring, with displacements of 0.2170 (7) and −0.2280 (7) Å, respectively. The $[ttcH_2]^-$ group is almost perpendicular to the phen planes, with angles between $ttcH_2$ and phen ligands *A*, *B* and *C* of 85.96 (7), 81.94 (7) and 85.86 (7)°, respectively.

In the crystal lattice of (I), the $ttcH_2$ molecular units are linked into one-dimensional chains by relatively strong intermolecular N—H···S hydrogen bonds.

Experimental

A solution of 1,10-phenanthroline monohydrate ($phen\cdot H_2O$; 0.4 g, 2 mmol) in ethanol (30 ml) was added to an ethanol solution (50 ml) of anhydrous magnesium(II) perchlorate (0.22 g, 1 mmol) with stirring at room temperature. The trisodium salt of trithiocyanuric acid nonahydrate ($ttcNa_3\cdot 9H_2O$; 0.4g, 1 mmol) was dissolved in water (5 ml) and added dropwise to this stirred solution. The solution turned light yellow in colour and was left to crystallize at ambient temperature. Initially, light-yellow crystals of (I) were obtained after 2 d. These were filtered off, washed with a small amount of ethanol and dried in air. The composition of this compound was proved by X-ray analysis. From the filtrate, a light-yellow precipitate was obtained after 2 d, and the composition of this compound was characterized by elemental analysis (EA1108 CHNS Analyzer, Fisons Instruments, Beverly, Massachusetts, USA) as $[Mg(phen)_3](ttcH)$. The Mg content was determined by chelatometric titration (found: C 63.1, H 3.4, N 16.8, S 12.8, Mg 3.4%; calculated: C 63.3, H 3.4, N 17.0, S 13.0, Mg 3.3%).

Crystal data

$[Na(C_{12}H_8N_2)_3](C_3H_2N_3S_3)$
$M_r = 739.86$
Monoclinic, $P2_1/n$
$a = 11.1273$ (9) Å
$b = 23.8687$ (15) Å
$c = 12.9417$ (7) Å
$\beta = 94.584$ (6)°
$V = 3426.2$ (4) Å^3
$Z = 4$

$D_x = 1.434$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5117 reflections
$\theta = 2.5$–26.4°
$\mu = 0.28$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.6 × 0.5 × 0.4 mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Rotation method, ω scans
14 962 measured reflections
5915 independent reflections
5060 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 25°$
$h = -8 \rightarrow 13$
$k = -28 \rightarrow 28$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.130$
$S = 0.99$
5915 reflections
574 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 3.8P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0033 (4)

Table 1
Selected geometric parameters (Å, °).

S1—C43	1.658 (3)	Na—N36	2.656 (3)
S2—C45	1.682 (2)	C43—N44	1.345 (3)
S3—C47	1.663 (2)	C43—N48	1.394 (3)
Na—N1	2.430 (2)	N44—C45	1.329 (3)
Na—N8	2.464 (2)	C45—N46	1.390 (3)
Na—N15	2.558 (3)	N46—C47	1.353 (3)
Na—N22	2.548 (2)	C47—N48	1.346 (3)
Na—N29	2.582 (3)		
N1—Na—N8	68.13 (7)	N29—Na—N36	63.08 (8)
N1—Na—N22	143.27 (9)	N44—C43—N48	118.4 (2)
N8—Na—N22	100.51 (8)	N44—C43—S1	124.02 (18)
N1—Na—N15	103.81 (8)	N48—C43—S1	117.55 (19)
N8—Na—N15	145.34 (10)	C45—N44—C43	119.3 (2)
N22—Na—N15	65.03 (8)	N44—C45—N46	120.0 (2)
N1—Na—N29	133.04 (9)	N44—C45—S2	122.74 (18)
N8—Na—N29	96.25 (8)	N46—C45—S2	117.28 (19)
N22—Na—N29	81.43 (8)	C47—N46—C45	122.8 (2)
N15—Na—N29	111.33 (8)	N48—C47—N46	114.2 (2)
N1—Na—N36	94.83 (8)	N48—C47—S3	123.39 (19)
N8—Na—N36	133.03 (9)	N46—C47—S3	122.39 (19)
N22—Na—N36	115.73 (8)	C47—N48—C43	124.1 (2)
N15—Na—N36	79.90 (8)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N46—H46···$S2^{i}$	0.85 (3)	2.46 (3)	3.298 (2)	170 (3)
N48—H48···$S3^{ii}$	0.91 (3)	2.44 (3)	3.336 (2)	165 (3)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, -y, 1 - z$.

All H atoms were located in a difference electron density map and refined freely [C—H = 0.93 (3)–1.03 (4) Å)].

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1175). Services for accessing these data are described at the back of the journal.

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