

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
Mn1	1/4	0.03581 (9)	0	0.0454 (3)
O1	0.3674 (2)	0.0211 (3)	0.1162 (2)	0.0541 (9)
O2	0.1833 (3)	-0.2428 (3)	0.1325 (2)	0.0810 (13)
O3	0.1886 (2)	-0.0929 (3)	0.0646 (2)	0.0657 (10)
N1	0.2308 (3)	-0.1594 (3)	0.1232 (2)	0.0485 (10)
N2	0.1610 (3)	0.1598 (3)	0.0495 (2)	0.0477 (10)
C1	0.3853 (3)	-0.0519 (4)	0.1735 (3)	0.0397 (11)
C2	0.4806 (3)	-0.0426 (4)	0.2442 (3)	0.0394 (10)
C3	0.5575 (3)	0.0214 (4)	0.2305 (3)	0.0491 (12)
C4	0.6445 (4)	0.0372 (5)	0.2945 (3)	0.0622 (15)
C5	0.6568 (4)	-0.0090 (5)	0.3745 (4)	0.071 (2)
C6	0.5816 (5)	-0.0725 (5)	0.3898 (4)	0.081 (2)
C7	0.4946 (4)	-0.0892 (5)	0.3253 (3)	0.061 (2)
C8	0.3241 (3)	-0.1419 (4)	0.1769 (3)	0.0478 (12)
C9	0.2051 (4)	0.2286 (5)	0.1125 (4)	0.069 (2)
C10	0.1550 (5)	0.2979 (6)	0.1518 (4)	0.082 (2)
C11	0.0534 (5)	0.3006 (5)	0.1252 (4)	0.070 (2)
C12	0.0035 (4)	0.2317 (5)	0.0595 (4)	0.0618 (15)
C13	0.0612 (4)	0.1640 (5)	0.0245 (3)	0.0559 (14)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Mn1—O1	2.118 (3)	O3—N1	1.257 (4)
Mn1—O3 <sup>1</sup>	2.175 (3)	N1—C8	1.361 (5)
Mn1—N2	2.228 (4)	C1—C8	1.397 (6)
O1—C1	1.253 (5)	C1—C2	1.492 (5)
O2—N1	1.242 (4)		
O1—Mn1—O1 <sup>1</sup>	170.3 (2)	C1—O1—Mn1	130.8 (3)
O1—Mn1—O3	80.13 (11)	N1—O3—Mn1	131.1 (3)
O1 <sup>1</sup> —Mn1—O3	92.80 (12)	O2—N1—O3	117.7 (4)
O3 <sup>1</sup> —Mn1—O3	87.6 (2)	O2—N1—C8	119.7 (4)
O1—Mn1—N2	96.52 (13)	O3—N1—C8	122.6 (4)
O3—Mn1—N2	89.80 (13)	O1—C1—C8	125.8 (4)
O1—Mn1—N2 <sup>1</sup>	90.10 (12)	O1—C1—C2	117.3 (4)
O3—Mn1—N2 <sup>1</sup>	169.74 (12)	C8—C1—C2	116.9 (4)
N2—Mn1—N2 <sup>1</sup>	94.4 (2)	N1—C8—C1	125.5 (5)

Symmetry code: (i)  $\frac{1}{2} - x, y, -z$ .

The crystals decompose slowly upon removal from their mother liquid. The sample was covered with a thin layer of epoxy. There was no significant decay during the course of data collection. The crystals are relatively weak scatterers. Cautious data collection procedures were used. Measured absorption corrections were applied to the data set. Eight complete  $\psi$  scans were used, along with three  $\psi$  scans of scattering vectors in general directions. The crystal was indexed with a body-centred monoclinic cell, using the shortest repeats in the  $ac$  plane as the  $a$  and  $c$  axes. The use of this 'more reduced' cell, which also has the least obtuse possible  $\beta$  angle for this lattice, is intended to minimize correlation in the refinement of the structure. The symmetry operations used for  $I2/a$  were  $(x, y, z)$ ,  $(\frac{1}{2} - x, y, -z)$ ,  $(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z)$ ,  $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ ,  $(-x, -y, -z)$ ,  $(\frac{1}{2} + x, -y, z)$ ,  $(\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z)$  and  $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ . During data collection, variable scan speeds were used, but final scans were forced for all reflections. Thus, the weakest reflections were gathered at the slowest scan speed. The solution and refinement of the structure proceeded routinely. All non-H atoms were located by direct methods. All eleven H atoms were seen in a difference Fourier map, and all were refined freely. Anisotropic displacement parameters were used for all non-H atoms.

Data collection: *CAD-4-PC* (Enraf-Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure:

*SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1273). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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**[Cr{tren(imp<sub>y</sub>)<sub>3</sub>}] (ClO<sub>4</sub>)<sub>3</sub>, where  
tren(imp<sub>y</sub>)<sub>3</sub> = N[CH<sub>2</sub>CH<sub>2</sub>N=C(H)(py)]<sub>3</sub>**

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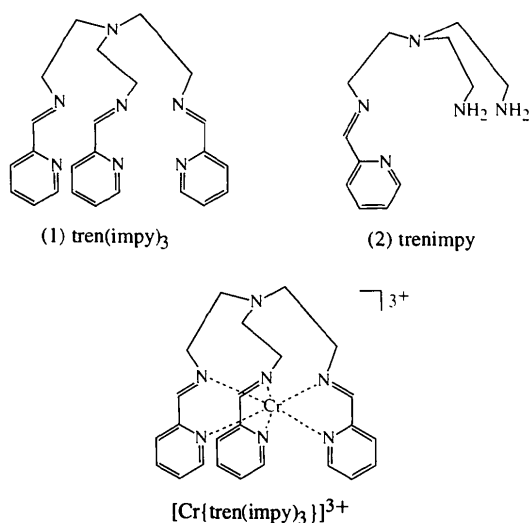
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## Abstract

The structure of {tris[4-(2-pyridyl)-3-aza-3-butenyl]-amine}chromium triperchlorate, [Cr{tren(imp<sub>y</sub>)<sub>3</sub>}] (ClO<sub>4</sub>)<sub>3</sub>, [Cr(C<sub>24</sub>H<sub>27</sub>N<sub>7</sub>)](ClO<sub>4</sub>)<sub>3</sub>, where tren(imp<sub>y</sub>)<sub>3</sub> is N[CH<sub>2</sub>CH<sub>2</sub>N=C(H)(py)]<sub>3</sub>, consists of [Cr{tren(imp<sub>y</sub>)<sub>3</sub>}]<sup>3+</sup> cations in which the Cr<sup>III</sup> centre adopts distorted octahedral coordination geometry. The trigonal twist angle of 52° is close to that expected for octahedral Cr<sup>III</sup> and there is little evidence suggesting coordination of the apical N atom of the tris(2-aminoethyl)-amine backbone of the ligand.

### Comment

The coordination chemistry of tren(impy)<sub>3</sub>, N[CH<sub>2</sub>CH<sub>2</sub>-N=C(H)(py)]<sub>3</sub>, (1), has been little explored apart from work on divalent metal ions, which include Ni<sup>II</sup> (Wilson & Rose, 1968), Fe<sup>II</sup> (Mealli & Lingafelter, 1970), Mn<sup>II</sup>, Fe<sup>II</sup>, Co<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> (Kirchner *et al.*, 1987), and Tc<sup>II</sup> (Thomas, Davidson & Jones, 1991). One driving force for these investigations was the potential for forming heptacoordinate complexes and hence the concentration of efforts on the larger divalent metal ions rather than trivalent ions. We have been interested in the coordination chemistry of pentadentate ligands derived from tren [tris(2-aminoethyl)amine]. An example of such a ligand is trenimpy, (2). In the course of attempts to prepare Cr<sup>III</sup> complexes of (2), a product was isolated with the composition [Cr{tren(impy)<sub>3</sub>}]ClO<sub>4</sub><sub>3</sub>. The structure of this complex is presented here.



The product initially crystallized from reaction mixtures prepared by mixing a solution of trenimpy, prepared as described previously (McLachlan *et al.*, 1994), with a solution of Cr<sup>2+</sup> in perchlorate media (Merakis, Murphy, Spiccia, Bequin & Marty, 1988). The product arises either because of the small amounts of the tris(imine) ligand in the synthesis or by the metal-catalyzed hydrolysis and rearrangement of trenimpy. Some evidence for the metal-catalyzed rearrangement of trenimpy to tren(impy)<sub>3</sub> was obtained in the case of Mn<sup>II</sup> (McLachlan, 1994). In the case of Cu<sup>II</sup>, the reaction of tren(impy)<sub>3</sub> with Cu<sup>II</sup> salts results in hydrolysis of the ligand. In fact, [Cu(trenimpy)]<sup>2+</sup> is produced as the stable product (Kirchner *et al.*, 1987), probably because of the strong preference of Cu<sup>II</sup> to form stable five-coordinate complexes with this type of pentadentate ligand (McLachlan, Fallon, Martin & Spiccia, 1995). Template synthesis about Cr<sup>III</sup> was found to be effective in producing [Cr{tren(impy)<sub>3</sub>}]ClO<sub>4</sub><sub>3</sub>. The reaction of [Cr(tren)Cl<sub>2</sub>]Cl with 3 mol equivalents of 2-pyridine-

carboxyaldehyde in methanol followed by addition of an aqueous solution of sodium perchlorate and work-up gave the product in better but still relatively low yield. Elemental analyses were consistent with the composition [Cr{tren(impy)<sub>3</sub>}]ClO<sub>4</sub><sub>3</sub>. The IR spectrum showed a band at 1636 cm<sup>-1</sup> due to the C=N stretches, bands due to the skeletal vibrations of the pyridine ring in the region 1400–1600 cm<sup>-1</sup> and most importantly no N—H stretching bands in the 3000–3500 cm<sup>-1</sup> region.

Fig. 1 shows the structure of the complex cation, [Cr{tren(impy)<sub>3</sub>}]<sup>3+</sup>. The primary coordination sphere of Cr<sup>III</sup> is composed of three pyridyl N atoms and three imine N atoms of the tren backbone. The three Cr—N(pyridyl) distances are equivalent and in the normal range for Cr<sup>III</sup> complexes of polydentate pyridyl ligands (*e.g.* Larsen, Michelsen & Pedersen, 1986; Gafford & Holwerda, 1989; Stearns & Armstrong, 1992). The Cr—N(imine) distances are also typical for this type of N-atom donor (Orpen *et al.*, 1989). Kirchner *et al.* (1987) have found systematic variations in these distances for a range of divalent metal ions. The Cr—N(3) distance is much longer [3.155(5) Å] indicating weak, if any, interaction with the metal centre. In the Tc<sup>II</sup> complex, although this distance is quite long [2.933(7) Å] there was indirect evidence from the angles about N(3) indicating that the lone pair on the tertiary N atom was pointing towards the Tc<sup>II</sup> centre (Thomas, Davidson & Jones, 1991). In the Cr<sup>III</sup> complex, the angles about the cap N atom [N(3)] are considerably enlarged from the expected tetrahedral angles and are, in fact, larger and closer to 120° than those found for the Tc<sup>II</sup> complex. This indicates that greater repulsion exists between N(3) and Cr<sup>III</sup> than in the Tc<sup>II</sup> case. The trigonal twist angles which span each pair of imine and pyridyl N atoms are 52° and are somewhat lower than expected for ideal octahedral geometry (60°) but considerably

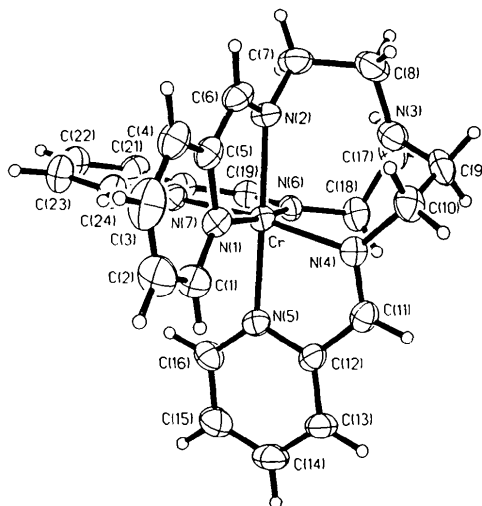


Fig. 1. Structure of the title complex showing the stereochemistry of the [Cr{tren(impy)<sub>3</sub>}]<sup>3+</sup> cation (40% ellipsoid probability level).

removed from those expected in complexes with trigonal prismatic geometry (0°). In fact, the twist angles in the Cr<sup>III</sup> complex are among the largest observed (Thomas, Davidson & Jones, 1991). The bite angles of the imine pyridyl arm are *ca* 79°, significantly reduced from 90° but larger than those found for the Tc<sup>II</sup> analogue where a short Tc—N(cap) distance was found. The open N(imine)—Cr—N(imine) angles are much closer to 90° than those observed in the Tc<sup>II</sup> system. The Cr—N—C angles about each imine N atom are slightly enlarged from 120° while those about each pyridine N atom are slightly lower than 120°. Overall, these considerations of the [Cr{tren(imp<sub>y</sub>)<sub>3</sub>}]<sup>3+</sup> structure indicate that the geometry of the complex is best described as distorted octahedral.

**Experimental**

[Cr(tren)Cl<sub>2</sub>]Cl was prepared by the literature method (Zipp & Madan, 1976). This compound (1.5 mmol, 0.46 g) was suspended in 60 ml of methanol; pyridine-2-carboxaldehyde (4.5 mmol, 0.48 g) was added and the mixture refluxed for 3–4 h. An aqueous solution of sodium perchlorate (2 g in 20 ml of water) was added and the volume of the solution was reduced to *ca* 20 ml. The product, [Cr{tren(imp<sub>y</sub>)<sub>3</sub>}(ClO<sub>4</sub>)<sub>3</sub>], precipitated on standing in a refrigerator at 275 K. Yield 0.26 g. Elemental analysis: found C 37.8, H 3.7, N 12.7, Cr 6.9%; C<sub>24</sub>H<sub>27</sub>Cl<sub>3</sub>CrN<sub>7</sub>O<sub>12</sub> requires C 37.7, H 3.6, N 12.8, Cr 6.8%. Selected IR bands (cm<sup>-1</sup>): 1636 *m* (C=N imine), 1602 *s* (pyridyl ring skeletal vibration). A small amount of crystals with the same analytical data and suitable for X-ray diffraction studies were obtained as a by-product of the attempted synthesis of [Cr(trenimp<sub>y</sub>)Cl](ClO<sub>4</sub>)<sub>2</sub>. The crystal density *D<sub>m</sub>* was measured by flotation in C<sub>2</sub>H<sub>2</sub>Br<sub>4</sub>/CCl<sub>4</sub>.

*Crystal data*

[Cr(C <sub>24</sub> H <sub>27</sub> N <sub>7</sub> )](ClO <sub>4</sub> ) <sub>3</sub>	Mo K $\alpha$ radiation
<i>M<sub>r</sub></i> = 763.9	$\lambda$ = 0.71073 Å
Monoclinic	Cell parameters from 30 reflections
<i>P</i> <sub>2</sub> / <i>c</i>	$\theta$ = 3–13°
<i>a</i> = 18.472 (4) Å	$\mu$ = 0.68 mm <sup>-1</sup>
<i>b</i> = 13.207 (2) Å	<i>T</i> = 293 K
<i>c</i> = 13.592 (2) Å	Prismatic
$\beta$ = 107.87 (1)°	0.29 × 0.29 × 0.24 mm
<i>V</i> = 3156 (1) Å <sup>3</sup>	Wine red
<i>Z</i> = 4	
<i>D<sub>x</sub></i> = 1.61 Mg m <sup>-3</sup>	
<i>D<sub>m</sub></i> = 1.60 (1) Mg m <sup>-3</sup>	

*Data collection*

Nicolet R3m/V diffractometer	<i>R</i> <sub>int</sub> = 0.023
$\omega$ scans	$\theta$ <sub>max</sub> = 25°
Absorption correction: analytical	<i>h</i> = -21 → 20
<i>T</i> <sub>min</sub> = 0.832, <i>T</i> <sub>max</sub> = 0.884	<i>k</i> = -1 → 15
7131 measured reflections	<i>l</i> = -1 → 16
5586 independent reflections	3 standard reflections monitored every 197 reflections
3317 observed reflections	intensity decay: none
[ <i>F</i> > 6 $\sigma$ ( <i>F</i> )]	

*Refinement*

Refinement on <i>F</i>	$w = 1/[\sigma^2(F_o) + 0.00741F_o^2]$
<i>R</i> = 0.056	( $\Delta/\sigma$ ) <sub>max</sub> = 0.004
<i>wR</i> = 0.074	$\Delta\rho$ <sub>max</sub> = 1.02 e Å <sup>-3</sup>
<i>S</i> = 1.83	$\Delta\rho$ <sub>min</sub> = -0.48 e Å <sup>-3</sup>
3313 reflections	Atomic scattering factors from SHELXTL-Plus (Sheldrick, 1991)
424 parameters	
H atoms: see below	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cr	0.25855 (5)	0.52190 (7)	0.17161 (7)	0.0323 (3)
N(1)	0.2802 (3)	0.4799 (4)	0.3235 (3)	0.037 (2)
N(2)	0.1632 (3)	0.5756 (4)	0.2007 (4)	0.040 (2)
N(3)	0.1977 (3)	0.7389 (4)	0.0895 (4)	0.048 (2)
N(4)	0.3273 (3)	0.6458 (4)	0.2180 (3)	0.037 (2)
N(5)	0.3601 (3)	0.4668 (4)	0.1599 (3)	0.037 (2)
N(6)	0.2239 (3)	0.5479 (3)	0.0164 (3)	0.035 (2)
N(7)	0.1975 (3)	0.3915 (4)	0.1170 (3)	0.036 (2)
C(1)	0.3417 (4)	0.4355 (5)	0.3856 (5)	0.048 (2)
C(2)	0.3468 (4)	0.4096 (6)	0.4867 (5)	0.062 (3)
C(3)	0.2881 (5)	0.4313 (6)	0.5241 (5)	0.066 (3)
C(4)	0.2242 (4)	0.4790 (5)	0.4613 (5)	0.049 (2)
C(5)	0.2221 (3)	0.5029 (5)	0.3620 (5)	0.040 (2)
C(6)	0.1593 (3)	0.5554 (5)	0.2900 (5)	0.043 (2)
C(7)	0.1008 (3)	0.6326 (5)	0.1275 (5)	0.054 (3)
C(8)	0.1272 (4)	0.7396 (5)	0.1163 (6)	0.061 (3)
C(9)	0.2588 (4)	0.8002 (5)	0.1528 (5)	0.053 (3)
C(10)	0.3035 (4)	0.7449 (5)	0.2469 (5)	0.051 (3)
C(11)	0.3949 (3)	0.6332 (5)	0.2148 (5)	0.044 (2)
C(12)	0.4156 (3)	0.5377 (5)	0.1808 (4)	0.040 (2)
C(13)	0.4855 (3)	0.5190 (5)	0.1676 (5)	0.050 (2)
C(14)	0.4983 (4)	0.4249 (6)	0.1331 (6)	0.059 (3)
C(15)	0.4432 (4)	0.3535 (6)	0.1126 (5)	0.058 (3)
C(16)	0.3746 (4)	0.3761 (5)	0.1281 (5)	0.046 (2)
C(17)	0.1916 (4)	0.7251 (5)	-0.0182 (5)	0.057 (3)
C(18)	0.2414 (4)	0.6406 (5)	-0.0341 (5)	0.049 (2)
C(19)	0.1836 (3)	0.4793 (5)	-0.0390 (4)	0.040 (2)
C(20)	0.1652 (3)	0.3906 (5)	0.0122 (4)	0.040 (2)
C(21)	0.1201 (3)	0.3125 (5)	-0.0387 (5)	0.049 (3)
C(22)	0.1059 (4)	0.2331 (6)	0.0182 (6)	0.060 (3)
C(23)	0.1387 (4)	0.2317 (5)	0.1230 (6)	0.058 (3)
C(24)	0.1846 (4)	0.3128 (5)	0.1697 (5)	0.050 (3)
O(1)	0.3031 (1)	0.3944 (1)	0.8241 (1)	0.056 (1)
O(2)	0.2711 (3)	0.3266 (4)	0.8808 (4)	0.082 (3)
O(3)	0.2422 (3)	0.4489 (5)	0.7537 (4)	0.091 (3)
O(4)	0.3424 (3)	0.3397 (5)	0.7676 (4)	0.085 (3)
O(5)	0.3524 (3)	0.4628 (5)	0.8940 (4)	0.099 (3)
O(6)	0.4361 (1)	0.6792 (1)	0.5226 (1)	0.056 (1)
O(7)	0.4709 (3)	0.6435 (5)	0.4497 (5)	0.096 (3)
O(8)	0.4379 (4)	0.7863 (4)	0.5266 (6)	0.111 (4)
O(9)	0.3567 (3)	0.6535 (5)	0.4812 (5)	0.101 (3)
O(10)	0.4642 (5)	0.6342 (8)	0.6156 (5)	0.170 (5)
O(11)	-0.0031 (1)	0.3765 (2)	0.2230 (2)	0.091 (1)
O(12)	-0.0596 (6)	0.4222 (8)	0.2486 (7)	0.175 (6)
O(13)	-0.0210 (5)	0.2687 (7)	0.2143 (7)	0.159 (5)
O(14)	0.0004 (4)	0.4136 (7)	0.1263 (5)	0.133 (4)
O(15)	0.0673 (3)	0.3829 (6)	0.2970 (5)	0.121 (3)

Table 2. Selected geometric parameters (Å, °)

Cr—N(1)	2.055 (5)	Cr—N(2)	2.046 (5)
Cr—N(4)	2.049 (5)	Cr—N(5)	2.063 (5)
Cr—N(6)	2.037 (5)	Cr—N(7)	2.067 (5)
N(1)—C(1)	1.325 (7)	N(1)—C(5)	1.364 (9)
N(2)—C(6)	1.267 (9)	N(2)—C(7)	1.477 (7)
N(3)—C(8)	1.456 (10)	N(3)—C(9)	1.440 (8)
N(3)—C(17)	1.444 (9)	N(4)—C(10)	1.472 (8)
N(4)—C(11)	1.273 (9)		

N(1)—Cr—N(2)	79.3 (2)	N(1)—Cr—N(4)	89.7 (2)
N(2)—Cr—N(4)	98.8 (2)	N(1)—Cr—N(5)	94.6 (2)
N(2)—Cr—N(5)	173.6 (2)	N(4)—Cr—N(5)	79.2 (2)
N(1)—Cr—N(6)	171.3 (2)	N(2)—Cr—N(6)	97.2 (2)
N(4)—Cr—N(6)	98.7 (2)	N(5)—Cr—N(6)	89.1 (2)
N(1)—Cr—N(7)	93.0 (2)	N(2)—Cr—N(7)	87.2 (2)
N(4)—Cr—N(7)	173.8 (2)	N(5)—Cr—N(7)	95.0 (2)
N(6)—Cr—N(7)	78.8 (2)	Cr—N(1)—C(1)	128.6 (5)
Cr—N(1)—C(5)	113.0 (3)	C(1)—N(1)—C(5)	118.4 (5)
Cr—N(2)—C(6)	114.7 (4)	Cr—N(2)—C(7)	125.9 (4)
C(6)—N(2)—C(7)	119.4 (6)	C(8)—N(3)—C(9)	116.3 (6)
C(8)—N(3)—C(17)	117.2 (5)	C(9)—N(3)—C(17)	118.6 (6)
Cr—N(4)—C(10)	125.7 (4)	Cr—N(4)—C(11)	114.0 (4)
C(10)—N(4)—C(11)	120.2 (5)	N(1)—C(1)—C(2)	121.5 (7)
N(1)—C(5)—C(4)	122.5 (5)	N(1)—C(5)—C(6)	114.2 (5)
N(2)—C(7)—C(8)	109.4 (5)	N(2)—C(6)—C(5)	118.7 (6)
N(3)—C(9)—C(10)	111.4 (5)	N(3)—C(8)—C(7)	111.0 (6)
N(4)—C(11)—C(12)	119.2 (6)	N(4)—C(10)—C(9)	109.9 (5)

Intensity data were corrected for Lorentz-polarization effects. A face-indexed numerical absorption correction was applied (Sheldrick, 1991) on seven crystal faces. The atomic scattering factors for neutral atoms were corrected for anomalous dispersion using the values of Sheldrick (1991). Four reflections (200, 011, 220,  $\bar{1}11$ ) were omitted from the final calculations due to extinction effects. Final refinement was by full-matrix least-squares employing anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms fixed at 0.08 Å<sup>2</sup> (positioned in geometrically idealized positions, C—H = 0.96 Å). The high displacement parameters (supplementary material) for the perchlorate anions are typical for this group for a refinement on room temperature data (see McLachlan, Fallon, Martin & Spiccia, 1995) and may be indicative of slight disorder. All calculations were performed on a MicroVAX 2000 computer.

Data collection: *Siemens P3/V Data Collection System* (Siemens, 1989). Cell refinement: *Siemens P3/V Data Collection System*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## A 2:1 Mixture of Tetrabutylammonium Bis(4,5-dimercapto-1,3-dithiole-2-thionato)-nickelate(II) and its 2-Selenone Analogue

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## Abstract

The X-ray analysis of the title compound, (C<sub>16</sub>H<sub>36</sub>N)<sub>2</sub>–[Ni(C<sub>3</sub>S<sub>4.67</sub>Se<sub>0.33</sub>)<sub>2</sub>], reveals that the anion contains 4,5-dimercapto-1,3-dithiole-2-thionato and 4,5-dimercapto-1,3-dithiole-2-selenato ligands in the ratio 2:1. The anion as a whole is planar and the central Ni atom has a square-planar coordination environment. The disorder in the tetrabutylammonium cation has been modelled to give acceptable geometric parameters.

## Comment

There has been particular interest in complexes of the DMIT ligand C<sub>3</sub>S<sub>5</sub><sup>2-</sup> (4,5-dimercapto-1,3-dithiole-2-thionato) since the discovery of superconductivity in salts of nickel and palladium DMIT complexes (Bousseau, Valade, Legros, Garbaskas & Interrante, 1986). Intermolecular interaction through S···S contacts is the basic requirement for high conductivity in this

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