

## Bis[(±)-*trans*-2-aminocyclohexylammonium] tetrathiomolybdate(VI) and *trans*-cyclohexane-1,4-diammonium tetrathiomolybdate(VI)

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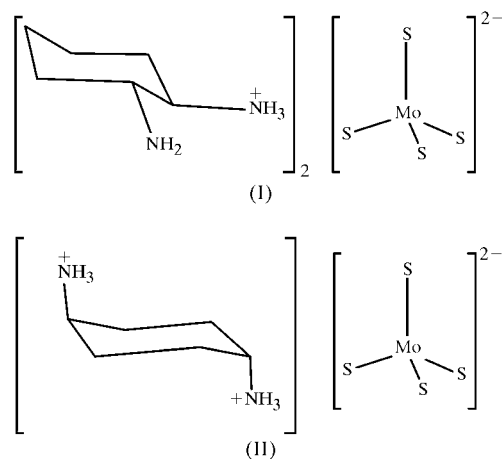
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The structures of the title complexes, (C<sub>6</sub>H<sub>15</sub>N<sub>2</sub>)<sub>2</sub>[MoS<sub>4</sub>], (I), and (C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>)<sub>2</sub>[MoS<sub>4</sub>], (II), can be described as consisting of discrete tetrahedral [MoS<sub>4</sub>]<sup>2-</sup> dianions that are linked to the organic ammonium cations *via* weak hydrogen-bonding interactions. The asymmetric unit of (I) consists of a single (±)-*trans*-2-aminocyclohexylammonium cation in a general position and an [MoS<sub>4</sub>]<sup>2-</sup> anion located on a twofold axis, while in (II), two crystallographically independent *trans*-cyclohexane-1,4-diammonium cations located on centres of inversion and one [MoS<sub>4</sub>]<sup>2-</sup> anion in a general position are found. The differing dispositions of the amine functionalities in the organic cations in the title complexes lead to different crystal packing arrangements in (I) and (II).

### Comment

The chemistry of Mo/S compounds is currently a frontier area of research because of the importance of MoS<sub>2</sub> in both hydrodesulfurization (HDS) catalysis and nanomaterials. Recent interest in the chemistry of tetrathiomolybdate includes the use of (NH<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] as a precursor for the preparation of highly porous MoS<sub>2</sub>, which exhibits very high HDS activity (Skrabalak & Suslick, 2005). A few years ago, we initiated a programme aimed at the synthesis of novel precursors for sulfide materials and as part of this research we are investigating the synthesis, structural and thermal characterization of organic ammonium tetrathiomolybdates (Srinivasan *et al.*, 2004). For the synthesis of organic ammonium tetrathiomolybdates we have developed a convenient and general method, which involves the reaction of an organic amine with ammonium tetrathiomolybdate. In earlier work, we have demonstrated the structural flexibility of the [MoS<sub>4</sub>]<sup>2-</sup> ion, as it can exist in a variety of structural environments (Ellermeier *et al.*, 1999; Ellermeier & Bensch, 2001, 2002; Srinivasan *et al.*, 2001, 2004; Srinivasan, Dhuri, Näther &

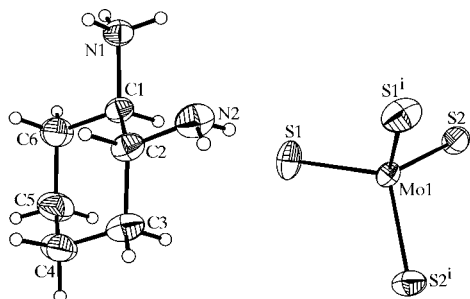
Bensch, 2005; Srinivasan, Näther & Bensch, 2005). The tetrathiomolybdate complexes reported by us exhibit weak hydrogen-bonding interactions between the organic ammonium cation and the anion. These hydrogen-bonding interactions can be altered by changing the steric bulk and the number of potential hydrogen-bonding donors attached to the N atoms of the organic amines. In an earlier report, we showed that (pipH<sub>2</sub>)[MoS<sub>4</sub>] (pip is piperazine) exhibits one of the longest known Mo—S bond distances [2.2114 (8) Å; Srinivasan *et al.*, 2004]. A careful analysis of the structures indicated a good correlation between the number of S⋯H interactions and the observed Mo—S bond lengths. In the present work, we have employed two isomeric cyclohexanediamines, namely (±)-*trans*-cyclohexane-1,2-diamine, *viz.* (±)-*trans*-1,2-cn, and *trans*-cyclohexane-1,4-diamine, *viz.* *trans*-1,4-cn, as the source for the organic cation for the reactions with (NH<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] and have structurally characterized two new complexes [(±)-*trans*-1,2-cnH]<sub>2</sub>[MoS<sub>4</sub>], (I), and (*trans*-1,4-cnH<sub>2</sub>)[MoS<sub>4</sub>], (II). The amines used here differ from the cyclic diamine pip in that the amine functional groups are outside the six-membered cyclohexane ring in the title compounds, whereas in pip, the amine N atoms form part of the six-membered ring. The title compounds are two additions to the growing list of structurally characterized tetrathiomolybdates. Interestingly, the diamine (±)-*trans*-1,2-cn is monoprotonated in (I), while the isomeric diamine *trans*-1,4-cn is diprotonated in (II).



The asymmetric unit of (I) contains the monoprotonated cation of (±)-*trans*-1,2-cn, which adopts a chair conformation, and the [MoS<sub>4</sub>]<sup>2-</sup> dianion (Fig. 1). The cation is located in a general position, while the anion is situated on a twofold axis. The MoS<sub>4</sub> tetrahedron is slightly distorted, with S—Mo—S angles ranging between 107.91 (3) and 110.85 (2)° (average 109.47°; Table 1). The Mo—S bond lengths range from 2.1751 (5) to 2.1876 (6) Å (Table 1), with a mean value of 2.1814 Å. Two of the bonds are shorter while the other two are longer than the average value of 2.1814 Å. The observed S⋯H distances are shorter than the sum of the van der Waals radii of S and H atoms (Bondi, 1964). All structural parameters of (I) are in good agreement with those reported for other compounds containing the [MoS<sub>4</sub>]<sup>2-</sup> ion, such as (enH<sub>2</sub>)-

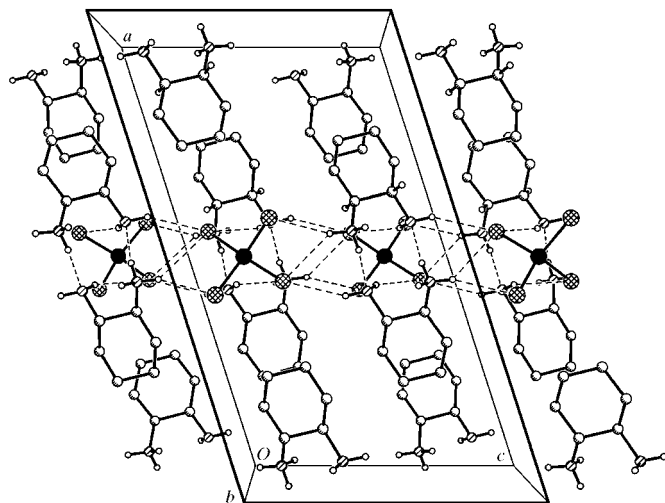
[MoS<sub>4</sub>] (en is ethylenediamine; Srinivasan *et al.*, 2001) and (1,3-pnH<sub>2</sub>)[MoS<sub>4</sub>] (1,3-pn is propane-1,3-diamine; Srinivasan, Dhuri, Näther & Bensch, 2005). As a result of the hydrogen-bonding interactions, the cations and anions in (I) are organized in a rod-like manner along [100], with the ammonium groups of the organic cations always pointing towards the S atoms of the anion. Hence, the sequence along this direction is  $\cdots[\text{MoS}_4]^{2-} \cdots \textit{trans}\text{-}1,2\text{-cnH} \cdots \textit{trans}\text{-}1,2\text{-cnH} \cdots [\text{MoS}_4]^{2-}$ . The special arrangement of the constituents may be viewed as layers within the (001) plane. Along [010] and [001], the anions and cations each form individual stacks. Each anion is surrounded by six cations, and five short S $\cdots$ H contacts ranging from 2.64 to 2.92 Å (Table 2) are observed. In addition, a very short N—H $\cdots$ N contact of 2.01 Å joins the cations to form pairs. The crystal packing of the resulting hydrogen-bonding network is shown in Fig. 2. The difference between the longest and shortest Mo—S bond,  $\Delta$ , in (I) is 0.0125 Å and is comparable to the  $\Delta$  value of 0.0111 Å observed for (enH<sub>2</sub>)[MoS<sub>4</sub>].

The structure of (II) consists of diprotonated *trans*-1,4-cn cations in a chair conformation and [MoS<sub>4</sub>]<sup>2-</sup> anions (Fig. 3). There are two crystallographically independent (*trans*-1,4-cnH<sub>2</sub>)<sup>2+</sup> cations and both are located on centres of inversion,



**Figure 1**

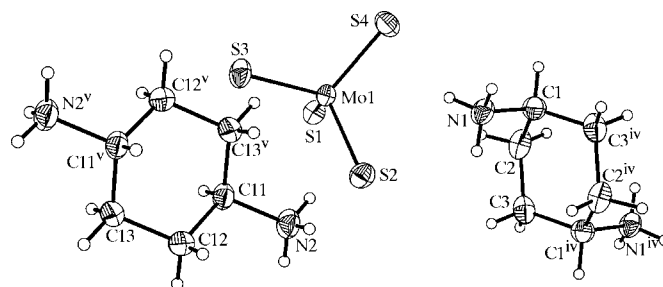
The crystal structure of (I), showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i)  $-x + 1, y, -z + \frac{1}{2}$ ]



**Figure 2**

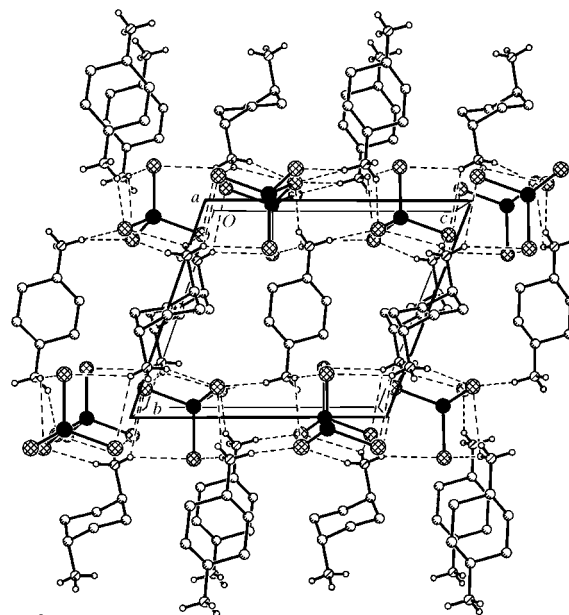
The packing of (I), viewed along the *b* axis; hydrogen bonds are shown as dashed lines.

while the anion is located in a general position. The MoS<sub>4</sub> tetrahedron is slightly distorted, with S—Mo—S angles ranging from 107.08 (2) to 110.81 (3)° (average 109.46°). The Mo—S bond lengths range from 2.1774 (7) to 2.1955 (7) Å (Table 3), with a mean Mo—S distance of 2.1865 Å. The geometric parameters are similar to those for (1,3-pnH<sub>2</sub>)[MoS<sub>4</sub>] and (1,4-bnH<sub>2</sub>)[MoS<sub>4</sub>] (1,4-bn is butane-1,4-diamine; Srinivasan, Näther & Bensch, 2005). Two of the Mo—S bonds are longer while the other two are shorter than the average of 2.1865 Å. In all, eight short intermolecular S $\cdots$ H contacts ranging from 2.47 to 2.81 Å are observed, and the S $\cdots$ H separations are shorter than the sum of the van der Waals radii (Bondi, 1964). The N $\cdots$ S distances for one cation range from 3.3539 (19) to 3.581 (2) Å, with N—H $\cdots$ S angles ranging between 121 and 167°, and for the second cation these distances are slightly shorter and lie between 3.287 (2) and 3.420 (2) Å, with N—H $\cdots$ S angles of 137–170°. Atom S4 has a single short contact, and atoms S1 and S3 have two short contacts each, while atom S2 is involved in three contacts. In general, the Mo—S bond lengths tend to be longer when the



**Figure 3**

The crystal structure of (II), showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (iv)  $-x + 2, -y + 3, -z + 2$ ; (v)  $-x + 1, -y + 1, -z + 1$ .]



**Figure 4**

The packing of (II), viewed along the *a* axis; hydrogen bonds are shown as dashed lines.

S···H contacts are shorter and the N—H···S angles are less acute (Table 4). As a result of the hydrogen-bonding interactions, alternating layers of cations and anions are formed in the crystallographic *ac* plane (Fig. 4). The value of  $\Delta$  is 0.0181 Å and is comparable to the values of 0.0183 and 0.0243 Å observed for (1,3-pnH<sub>2</sub>)[MoS<sub>4</sub>] and (1,4-bnH<sub>2</sub>)[MoS<sub>4</sub>], respectively. Since the amine functionalities in the organic cations in (I) and (II) are differently disposed, they form different numbers of hydrogen bonds, which leads to different crystal packings. The very short N—H···N contact in (I) joins the cations to form pairs. In contrast, two adjacent organic cations in (II) are linked *via* N—H···S bonds through an intervening [MoS<sub>4</sub>]<sup>2-</sup> anion. The observed  $\Delta$  values for (I) and (II) are in the range observed for tetrathiomolybdates derived from acyclic diamines such as en and 1,3-pn, whose  $\Delta$  values (0.0111 and 0.0183 Å) are much smaller than the  $\Delta$  value (0.0431 Å) observed for (pipH<sub>2</sub>)[MoS<sub>4</sub>].

## Experimental

Ammonium tetrathiomolybdate (260 mg, 1 mmol) was dissolved in distilled water (15–20 ml), a few drops of aqueous ammonia were added and the mixture was filtered. ( $\pm$ )-*trans*-1,2-cn (0.5 ml) was added to the clear red filtrate, and the reaction mixture was left aside for crystallization. After a day, red crystals of (I) separated slowly. The crystals were filtered off, washed with ice-cold water (2 ml) followed by isopropyl alcohol (10 ml) and diethyl ether (10 ml), and air dried (yield 70%). The use of *trans*-1,4-cn (114 mg) instead of ( $\pm$ )-*trans*-1,2-cn in the above reaction under identical conditions afforded (II) in 75% yield. Both compounds are air stable and analysed satisfactorily.

### Compound (I)

#### Crystal data

(C<sub>6</sub>H<sub>15</sub>N<sub>2</sub>)<sub>2</sub>[MoS<sub>4</sub>]  
*M<sub>r</sub>* = 454.58  
 Monoclinic, *C*2/*c*  
*a* = 19.279 (3) Å  
*b* = 9.4502 (11) Å  
*c* = 11.3308 (16) Å  
 $\beta$  = 107.736 (12)°  
*V* = 1966.2 (5) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.536 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 74 reflections  
 $\theta$  = 10–19°  
 $\mu$  = 1.09 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, red  
 0.1 × 0.09 × 0.08 mm

#### Data collection

Stoe AED-II four-circle diffractometer  
 $\omega$ - $\theta$  scans  
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)  
*T<sub>min</sub>* = 0.889, *T<sub>max</sub>* = 0.909  
 3593 measured reflections  
 2863 independent reflections  
 2357 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.017  
 $\theta_{\max}$  = 30.0°  
*h* = -27 → 25  
*k* = -13 → 2  
*l* = 0 → 15  
 4 standard reflections  
 frequency: 120 min  
 intensity decay: none

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.024  
*wR* (*F*<sup>2</sup>) = 0.061  
*S* = 1.04  
 2863 reflections  
 98 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 1.4007P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.45 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.00056 (14)

**Table 1**

Selected geometric parameters (Å, °) for (I).

Mo1—S1 <sup>i</sup>	2.1751 (5)	C1—C6	1.518 (2)
Mo1—S1	2.1751 (5)	C1—C2	1.530 (2)
Mo1—S2 <sup>i</sup>	2.1876 (6)	C2—C3	1.527 (3)
Mo1—S2	2.1876 (5)	C3—C4	1.518 (3)
N1—C1	1.4996 (19)	C4—C5	1.511 (3)
N2—C2	1.469 (2)	C5—C6	1.525 (3)
S1 <sup>i</sup> —Mo1—S1	108.41 (3)	C6—C1—C2	111.56 (14)
S1 <sup>i</sup> —Mo1—S2 <sup>i</sup>	109.41 (2)	N2—C2—C3	114.66 (16)
S1—Mo1—S2 <sup>i</sup>	110.85 (2)	N2—C2—C1	109.94 (14)
S1 <sup>i</sup> —Mo1—S2	110.85 (2)	C3—C2—C1	109.58 (15)
S1—Mo1—S2	109.41 (2)	C4—C3—C2	111.82 (18)
S2 <sup>i</sup> —Mo1—S2	107.91 (3)	C5—C4—C3	110.48 (18)
N1—C1—C6	110.27 (13)	C4—C5—C6	110.59 (19)
N1—C1—C2	109.52 (12)	C1—C6—C5	111.42 (17)

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

**Table 2**

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1N1···S2 <sup>ii</sup>	0.89	2.75	3.5762 (16)	155
N1—H1N1···S1 <sup>ii</sup>	0.89	2.86	3.4577 (17)	126
N1—H2N1···N2 <sup>i</sup>	0.89	2.01	2.898 (2)	171
N1—H3N1···S2 <sup>iii</sup>	0.89	2.66	3.5238 (17)	164
N2—H2N2···S1	0.89	2.92	3.7684 (14)	161
N2—H1N2···S1 <sup>iv</sup>	0.89	2.64	3.4193 (13)	146

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

### Compound (II)

#### Crystal data

(C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>)[MoS<sub>4</sub>]  
*M<sub>r</sub>* = 340.39  
 Triclinic, *P*1̄  
*a* = 7.0045 (12) Å  
*b* = 9.6833 (18) Å  
*c* = 10.530 (2) Å  
 $\alpha$  = 108.621 (10)°  
 $\beta$  = 92.564 (10)°  
 $\gamma$  = 106.240 (10)°  
*V* = 642.7 (2) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.759 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 84 reflections  
 $\theta$  = 20–38.5°  
 $\mu$  = 1.63 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, red  
 0.11 × 0.09 × 0.07 mm

#### Data collection

Stoe AED-II four-circle diffractometer  
 $\omega$ - $\theta$  scans  
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)  
*T<sub>min</sub>* = 0.832, *T<sub>max</sub>* = 0.887  
 4363 measured reflections  
 3747 independent reflections  
 2951 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.016  
 $\theta_{\max}$  = 30.0°  
*h* = -1 → 9  
*k* = -13 → 13  
*l* = -14 → 14  
 4 standard reflections  
 frequency: 120 min  
 intensity decay: none

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.022  
*wR* (*F*<sup>2</sup>) = 0.053  
*S* = 1.02  
 3747 reflections  
 118 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2 + 0.1519P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{Å}^{-3}$

**Table 3**  
Selected geometric parameters (Å, °) for (II).

Mo1—S4	2.1774 (7)	C1—C3 <sup>iv</sup>	1.529 (3)
Mo1—S1	2.1851 (6)	C2—C3	1.524 (3)
Mo1—S2	2.1881 (7)	N2—C11	1.495 (2)
Mo1—S3	2.1955 (7)	C11—C13 <sup>v</sup>	1.517 (3)
N1—C1	1.507 (2)	C11—C12	1.517 (3)
C1—C2	1.520 (3)	C12—C13	1.526 (3)
S4—Mo1—S1	110.12 (3)	C2—C1—C3 <sup>iv</sup>	111.68 (16)
S4—Mo1—S2	109.43 (3)	C1—C2—C3	113.67 (18)
S1—Mo1—S2	107.08 (2)	C2—C3—C1 <sup>iv</sup>	113.27 (17)
S4—Mo1—S3	110.81 (3)	N2—C11—C13 <sup>v</sup>	109.23 (16)
S1—Mo1—S3	108.91 (3)	N2—C11—C12	109.74 (17)
S2—Mo1—S3	110.42 (3)	C13 <sup>v</sup> —C11—C12	112.12 (17)
N1—C1—C2	111.10 (16)	C11—C12—C13	110.20 (17)
N1—C1—C3 <sup>iv</sup>	110.18 (17)	C11 <sup>v</sup> —C13—C12	110.70 (16)

Symmetry codes: (iv)  $-x + 2, -y + 3, -z + 2$ ; (v)  $-x + 1, -y + 1, -z + 1$ .**Table 4**  
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N1...S3 <sup>vi</sup>	0.89	2.65	3.3639 (19)	138
N1—H1N1...S4 <sup>vi</sup>	0.89	2.94	3.4559 (18)	118
N1—H2N1...S1 <sup>vii</sup>	0.89	2.52	3.398 (2)	167
N1—H3N1...S4	0.89	2.75	3.581 (2)	155
N1—H3N1...S2	0.89	2.81	3.3539 (19)	121
N2—H1N2...S2 <sup>viii</sup>	0.89	2.62	3.339 (2)	139
N2—H1N2...S1 <sup>viii</sup>	0.89	2.71	3.420 (2)	137
N2—H2N2...S3 <sup>vi</sup>	0.89	2.53	3.405 (2)	170
N2—H3N2...S2	0.89	2.47	3.287 (2)	153

Symmetry codes: (vi)  $-x + 1, -y + 2, -z + 2$ ; (vii)  $x + 1, y, z$ ; (viii)  $-x + 1, -y + 2, -z + 1$ .

H atoms were positioned with idealized geometry (C—H = 0.97 or 0.98 Å and N—H = 0.89 Å) and refined using a riding model, with  $U_{\text{iso}}(\text{H})$  fixed at  $1.2U_{\text{eq}}(\text{C}, \text{N}_{\text{amine}})$  and  $1.5U_{\text{eq}}(\text{N}_{\text{ammonium}})$ . In (I), the ammonium H atoms were allowed to rotate but not tip, and the amine

H atoms were located in a difference map but their bond lengths were set at ideal values.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1998); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1276). Services for accessing these data are described at the back of the journal.

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