The title proligand, C_{29}H_{34}N_{2}S_{4}, exhibits two kinds of intramolecular hydrogen bonds, N—H····S and C—H····S, described by the graph-set symbols S(6) and S(5), respectively. The structural parameters of the molecule suggest a partial electron delocalization involving the nitrogen lone pair, the cyclopentene ring and the carbodithioate group. In the crystal structure, the molecules are held together mainly by C—H····π and van der Waals interactions.

Comment

The development of nitrogen and sulfurated proligands are of great relevance for bioinorganic chemistry (Holm & Solomon, 2004). Frequently, the aim has been to synthesize low molecular weight model compounds in order to gain a better understanding of the role played by metal centres on the properties of metallobiomolecules (Ibers & Holm, 1980). There are a great variety of model complexes (Mandal et al., 1997; Kim et al., 2001; Anderson et al., 1997), which involve pseudo-tetrahedral metal coordination with two N- and two S-donor atoms. From the biomimetic point of view, these molecular analogues with specific metal-coordination environments are very attractive, because of their similarity to biological systems found in nature. Among these can be mentioned those observed in (i) blue copper proteins (Gray & Solomon, 1981), (ii) carbon monoxide dehydrogenase (Diekert, 1988) and (iii) zinc finger proteins (Lipscomb & Sträter, 1996). Pioneering synthetic studies with such a family of proligands and their metal complexes were carried out by Nag & Joardar (1975, 1976) and Bereman et al. (1979, 1981). These authors focused their attention on (N,S) proligands derived from 2-amino-1-cyclopentene-1-dithiocarboxylic acid. More recently, we have developed the synthesis of several ligands of the class ethyl-N,N’-alkyl-bis(2-amino-1-cyclopentene-carbodithioate) (Contreras et al., 2005) and 2,4-bis-(cyclohexane)dispiro-1,2,3,4,4a,5,6,7-octahydro-(1H,3H)-quinazoline-8-carbodithioate (Contreras et al., 2001).
The bond lengths in the S(6) rings have values (Table 1) typical of a conjugated system [average C—C = 1.39 Å and C—N = 1.320 Å] (Cambridge Structural Database; Version 5.25; Allen, 2002). These structural features suggest electron delocalization involving the nitrogen lone pair, the cyclopentene ring and the carbodithioate group. These distances agree with values previously reported in analogous compounds, such as methyl-N,N’-propyl-bis(2-amino-1-cyclopentenecarbodithioate), methyl-N,N’-(3,6-diazaoctane)-bis(2-amino-1-cyclopentenecarbodithioate), methyl-N,N’-diethyl-amino-bis(2-amino-1-cyclopentenecarbodithioate) (Sarkar & Gupta, 1981,1982a,b, respectively) and (R)-bis(N-phenylethyl-2-amino-1-cyclopentenemercaptomethyl)disulfide (Cea-
44,050 (10,800), 31,550 (10,900), 25,690 (16,400), 25,000 (14,600). The electronic absorption spectrum shows bands in the ultraviolet region assigned as $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the chromophoric groups present: $-C=C--K(benzene), -C=S + B(benzene), -C=N-- + C=S$ and $-H$. These bands displayed a bathochromic effect. IR (cm$^{-1}$): 3374 (v)/C$^3$ 4986 independent reflections and $\delta_{eq}(C,N)$. The 13C NMR spectra show the following values: $\delta$ 202.7 (C$5$-C$2$-H$_2$), 169.8 (N$-$C$=C$), 137.4, 129.3, 128.4, 127.1, 117.8, 42.9, 37.9, 33.3, 32.8, 20.6.

Crystal data

$C_{29}H_{34}N_2S_4$, $M_r = 538.82$, Triclinic, $\alpha = 7.8860$ (3) Å, $b = 12.427$ (3) Å, $c = 14.752$ (3) Å, $\alpha = 90.62$ (3)$^\circ$, $\beta = 94.24$ (3)$^\circ$, $\gamma = 101.25$ (3)$^\circ$, $V = 1413.6$ (5) Å$^3$.

Data collection

$\theta_{max} = 25.0^\circ$, 316 parameters, H atoms constrained.

Table 1

| Selected geometric parameters (Å, $^\circ$) |
|------------------------------------------|
| S1$-$C1 | 1.695 (3) |
| S2$-$C1 | 1.771 (3) |
| S3$-$C2 | 1.808 (3) |
| S4$-$C2 | 1.683 (3) |
| S5$-$C3 | 1.780 (3) |
| S6$-$C3 | 1.814 (3) |
| N1$-$C4 | 1.315 (3) |
| C1$-$C14 | 1.459 (3) |
| C1$-$S2$-$C7 | 105.12 (14) |
| C2$-$S4$-$C23 | 105.38 (14) |
| C3$-$N1$-$C14 | 125.1 (2) |
| C17$-$N2$-$C16 | 124.8 (2) |
| C21$-$C1$-$S1 | 126.2 (2) |
| C22$-$S1$-$S2 | 112.62 (2) |
| C1$-$S1$-$S2 | 121.15 (17) |
| C1$-$C2$-$C3 | 126.9 (2) |
| C1$-$C2$-$C6 | 125.2 (2) |
| C1$-$C3$-$C6 | 107.8 (2) |
| C1$-$C3$-$C4 | 122.8 (2) |
| C2$-$C3$-$C4 | 111.4 (2) |
| C4$-$C5$-$C4 | 105.2 (2) |
| C5$-$C6$-$C2 | 104.4 (2) |

Table 2

| Hydrogen-bond geometry (Å, $^\circ$). |
|-------------------------------------|
| D$-H$ ... A | D$-H$ | H$-A$ | D$-A$ | D$-H$ ... A |
| N1$-$H1 ... S1 | 0.86 | 2.29 | 3.018 (3) | 142 |
| N2$-$H2 ... S3 | 0.90 | 2.29 | 3.050 (2) | 138 |
| C7$-$H2B ... S1 | 0.97 | 2.66 | 3.140 (3) | 111 |
| C32$-$H23B ... S3 | 0.97 | 2.62 | 3.179 (3) | 117 |
| C14$-$H14A ... Cg3$^i$ | 0.97 | 2.99 | 3.673 (3) | 125 |
| C21$-$H21A ... Cg4$^a$ | 0.97 | 3.13 | 3.583 (38) | 110 |
| C21$-$H21B ... Cg4$^i$ | 0.97 | 3.13 | 3.583 (38) | 110 |

Symmetry codes: (i) $-x+1, -y+1, -z+2$. (ii) $-x, -y+1, -z+1$. Cg3 and Cg4 are the centroids of the C8$-$C13 and C24$-$C29 phenyl rings.

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