some possible degree of localization of unsaturation along the former Ru—Ru vector, although the evidence is not strong.

The structure is closely related to that reported for the 58 CVE cluster $Ru_3Pt(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}CO)_2$-$(CO)_7(PCy_3)$ (2), in which a three-electron donor phosphido group replaces the μ-allyl ligand (Powell, Brewer, Gulia & Sawyer, 1989). The major difference in the metal frameworks is that the M—M distances in the Pt—Ru(1)—Ru(3) face of the title cluster are slightly greater than found for the corresponding face in (2), presumably due to the differing bonding requirements of the PPh_2 versus the allyl ligand. The only other structurally characterized tetrahedral Ru_3Pt species is the 60 CVE cluster $Ru_3Pt\{\mu_3\text{-}\eta^4$-('Bu).C.C.C('Bu).$CH_2\}(CO)_8(dppe)$ which has Ru—Pt distances of 2.700 (3)–2.892 (3) Å and Ru—Ru distances of 2.770 (4)–2.904 (4) Å (Farrugia, MacDonald & Peacock, unpublished results).

Note added in proof: A similar $\mu\text{-}\eta^3$ allyl linkage acting as a three-electron donor has recently been reported [Housecroft, Johnson, Lewis, Lunniss, Owen & Raithby (1991). *J. Organomet. Chem.* **409**, 271–284].

References

BHADHURI, S., JOHNSON, B. F. G., KELLAND, J. W., LEWIS, J., RAITHBY, P. R., REHANI, S., SHELDRICK, G. M., WONG, K. & McPARTLIN, M. (1979). *J. Chem. Soc. Dalton Trans.* pp. 562–568.

EVANS, M., HURSTHOUSE, M., RANDALL, E. W., ROSENBERG, E., MILONE, L. & VALLE, M. (1972). *J. Chem. Soc. Chem. Commun.* pp. 545–546.

FARRUGIA, L. J. (1990). *Adv. Organomet. Chem.* **31**, 301–391.

FARRUGIA, L. J., HOWARD, J. A. K., MITRPRACHACHON, P., STONE, F. G. A. & WOODWARD, P. (1981). *J. Chem. Soc. Dalton Trans.* pp. 155–161.

GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.

ORPEN, A. G. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2509–2516.

POWELL, J., BREWER, J. C., GULIA, G. & SAWYER, J. F. (1989). *Inorg. Chem.* **28**, 4470–4476.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

WERNER, H. (1981). *Adv. Organomet. Chem.* **19**, 155–182.

Structure of 2,3-Dicyclohexyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraaza-cyclopent[cd]indene-1(2H),4(2H)-diselone

By David G. Billing, Jan C. A. Boeyens, Louis Denner, Michael D. Hellyar, Long-Li Lai, Anthony J. Matthee and David H. Reid

Structural Chemistry Group, Department of Chemistry, University of the Witwatersrand, Wits 2050, Johannesburg 2001, South Africa

Abstract. $C_{18}H_{28}N_4SSe_2$, $M_r = 490.435$, monoclinic, $P2_1/c$, $a = 6.455$ (9), $b = 19.990$ (6), $c = 16.43$ (1) Å, $\beta = 101.4$ (10)°, $V = 2078.90$ Å^3, $Z = 4$, $D_x = 1.57$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 35.49 cm^{-1}, $F(000) = 992$, $T = 293$ K, $wR = 0.0567$ for 2727 reflections with $F \geq 3\sigma(F)$. The molecule possesses elongated S—N bonds of 1.935 (7) and 1.931 (7) Å, an N—S—N angle of 164.8 (3)° and C=Se bond lengths of 1.844 (9) and 1.826 (9) Å.

Introduction. The determination of the structure of the title compound [(2) R = cyclohexyl] arose from attempts to synthesize new types of 1,6,6aλ^4-triheterapentalene structure (Mitchell & Reid, 1982; Nicol, 1983; Rhodes, 1987; Lai, 1990). 1,6,6aλ^4-Triheterapentalenes contain a sequence of three heteroatoms of Groups V and VI (O, S, Se, Te, NR) in which the two bonds linking adjacent heteroatoms in the sequence are characteristically long, being up to ca 15% longer than the corresponding two-centre two-electron covalent bonds (Mitchell & Reid, 1982; and earlier work and references cited therein). We have found that the 1,2,4-thiadiazolo[4,5-a]-pyrimidine (2), synthesized by the reaction of 5-amino-3-methyl-1,2,4-thiadiazole with 1,3-dibromopropane (Nicol, 1983; Lai, 1990), reacts with isoselenocyanates in boiling toluene with elimination of acetonitrile and concomitant addition of two molecules of the isoselenocyanate to give products which, on the basis of elemental composition, ^{1}H and ^{13}C NMR spectra, and mechanistic considerations, seemed likely to possess structure (2) or structure (3). The same products were also obtained, together with 2,4-dinitrotoluene, by reaction of the tetrahydropyrimidine (4) with the appropriate isoselenocyanates in dichloromethane at room temperature. We now report that the product from the reaction of compound (1) or (4) with cyclohexyl isoselenocyanate

possesses the N—S—N triheterapentalene structure [(2) R = cyclohexyl] on the basis of an X-ray single-crystal structure determination.

(1)

(2)

(3)

(4)

(5)

(6)
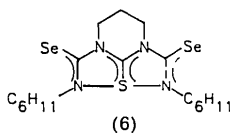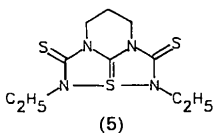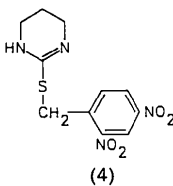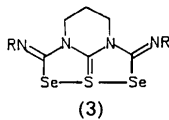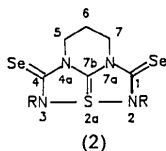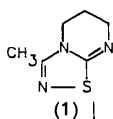
Experimental. The title compound crystallized from acetonitrile–dichloromethane (2:1) as pale-yellow needle-shaped crystals, m.p. 445–453 K (decomposition). Analysis: calculated for $C_{18}H_{28}N_4SSe_2$: C 44.08, H 5.76, N 11.42%; found: C 44.16, H 5.74, N 11.52%. ^1H NMR (200 MHz, CDCl$_3$): δ 1.24–2.20 (m, 20 H, cyclohexyl CH$_2$), 2.38 (quint, 2H, 6-CH$_2$), 4.35–4.48 (m, 2H, cyclohexyl CH), and 4.57 (t, 4H, 5- and 7-CH$_2$). ^{13}C NMR (80 MHz, CDCl$_3$): δ 19.74, 25.33, 25.48 and 32.48 (cyclohexyl CH$_2$ and 6-CH$_2$), 47.13 and 60.56 (cyclohexyl CH, 5-CH$_2$ and 7-CH$_2$), 156.07, (7b-CH$_2$), and 165.04 (1-C=Se and 4-C=Se).

A needle-shaped crystal fragment of dimensions 1.18 × 0.18 × 0.18 mm was cleaved from a larger crystal and sealed into a Lindemann capillary. After preliminary photographic examination crystal and intensity data (ω–2θ mode) were measured with an Enraf–Nonius CAD-4 diffractometer. Accurate cell constants, space group $P2_1/c$, were refined by least squares on the basis of 25 measurements in the range $10 \le \theta \le 19°$. Data reduction consisted of correction for background scattering, an estimated 7.1% crystal decay, Lp factors and absorption by empirical procedures; transmission factors between 80 and 100%. 4741 measured intensities were merged to produce a unique set of 3863 with an internal consistency index of 0.02, within the range $3 \le \theta \le 27°$; h, k, $l - 8 \to 8$, $0 \to 25$, $0 \to 20$. Treating all intensities $I < 3\sigma(I)$ as unobserved, left a total of 2727 used for the least-squares refinement of 227 parameters.

The structure was solved by direct methods and refined by full-matrix least squares, using SHELX76 (Sheldrick, 1978) for all computations. All H atoms, including those revealed in difference maps, were placed in geometrically calculated positions and refined in riding mode with a common isotropic temperature factor. All non-H atoms were refined anisotropically. At the termination of refinement no parameter shifts exceeded 0.001σ and residual densities were within the range -1.20–0.8 e Å^{-3}. The conventional $R = 0.064$. A weighting scheme based on counting statistics, $w \propto 1/\sigma^2(F)$, was used, $wR = 0.057$.

Discussion. Final atomic coordinates and bond distances and angles are listed in Tables 1 and 2.* The structure of 2,3-dicyclohexyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),-4(2H)-diselone [(2) R = cyclohexyl] is shown in Fig. 1, which also defines the crystallographic numbering scheme. The bicyclic triheterapentalene unit is nearly planar, with maximum deviations from planarity not exceeding 0.02 Å. The cyclohexyl rings exist in chair conformations. The compound shows the structural features characteristic of 1,6,6aλ^4-triheterapenta-lenes. Thus the S—N bond lengths of 1.935 (7) and 1.931 (7) Å are greater by 11.2 and 11.0%, respectively, than the two-centre two-electron S—N covalent bond length (1.74 Å) based on the sum of the covalent radii of sulfur and nitrogen (Pauling, 1960). These S—N bond lengths fall within the range (1.83–1.98 Å) found for S—N bonds in six other triheterapentalenes containing an N—S—N sequence (Birknes & Hordvik, 1982; Goerdeler & Löbach, 1979; Hordvik & Julshamn, 1972; Iwasaki & Akiba, 1981, 1984; Matsumura, Tomura, Toriumi & Yoneda, 1986). The N—S—N bond angle of 164.8 (3) Å in the title compound lies in the range previously found for the N—S—N angle in these six triheterapentalenes. The lengths of corresponding bonds and the size of corresponding bond angles in the two halves of the triheterapentalene framework of [(2) R = cyclohexyl] are very similar, differing from one another at most by 0.039 Å and 2.9°, respectively. The lengths of the C—C, C—N, C—S and N—S bonds are very similar to those of the corresponding bonds in the thiocarbonyl analogue (5) (Matsumura, Tomura, Toriumi & Yoneda, 1986). Bond angles in the title compound also differ very little from the corresponding bond angles in (5).

The C=Se bond lengths of 1.844 (9) for C(1)= Se(1) and 1.826 (9) Å for C(5)=Se(2) lie midway between the length of a carbon–selenium single bond (1.97 Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) (1.94 Å, sum of the covalent radii of

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}
Se(1)	1478 (2)	2777 (1)	3898 (1)	61 (0)
Se(2)	8540 (2)	−173 (1)	6308 (1)	61 (0)
S	3711 (4)	1511 (1)	6211 (1)	44 (1)
N(1)	2182 (11)	2200 (3)	5511 (4)	45 (2)
N(2)	4226 (11)	1776 (4)	4691 (4)	48 (2)
N(3)	6292 (11)	886 (4)	5396 (4)	49 (2)
N(4)	5561 (11)	784 (4)	6655 (4)	43 (2)
C(1)	2695 (15)	2236 (5)	4770 (5)	51 (2)
C(2)	5150 (16)	1697 (5)	3937 (5)	77 (3)
C(3)	7269 (16)	1361 (6)	4182 (6)	91 (3)
C(4)	7317 (14)	745 (5)	4689 (5)	71 (3)
C(5)	6700 (13)	531 (4)	6155 (5)	53 (2)
C(6)	4831 (14)	1376 (4)	5354 (5)	47 (2)
C(7)	5679 (13)	540 (5)	7520 (5)	46 (2)
C(8)	3648 (14)	602 (7)	7807 (6)	84 (4)
C(9)	3891 (15)	366 (6)	8705 (6)	90 (4)
C(10)	5580 (17)	734 (6)	9274 (6)	83 (4)
C(11)	7705 (17)	665 (6)	8988 (6)	98 (4)
C(12)	7483 (17)	922 (6)	8086 (6)	107 (4)
C(13)	656 (13)	2648 (4)	5799 (5)	49 (2)
C(14)	1760 (16)	3304 (5)	6133 (6)	77 (3)
C(15)	161 (17)	3780 (5)	6396 (6)	86 (3)
C(16)	−1054 (16)	3455 (5)	7006 (6)	67 (3)
C(17)	−2040 (14)	2801 (5)	6688 (6)	74 (3)
C(18)	−413 (14)	2313 (5)	6431 (5)	58 (3)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(1)—Se(1)	1.844 (9)	C(5)—Se(2)	1.826 (9)
N(1)—S	1.935 (7)	N(4)—S	1.931 (7)
C(6)—S	1.726 (8)	C(1)—N(1)	1.324 (9)
C(13)—N(1)	1.477 (9)	C(1)—N(2)	1.375 (11)
C(2)—N(2)	1.485 (10)	C(6)—N(2)	1.345 (10)
C(4)—N(3)	1.473 (9)	C(5)—N(3)	1.414 (10)
C(6)—N(3)	1.352 (10)	C(5)—N(4)	1.307 (10)
C(7)—N(4)	1.489 (10)	C(3)—C(2)	1.505 (12)
C(4)—C(3)	1.483 (12)	C(12)—C(7)	1.542 (12)
C(8)—C(7)	1.484 (11)	C(10)—C(9)	1.484 (13)
C(9)—C(8)	1.527 (12)	C(12)—C(11)	1.548 (12)
C(11)—C(10)	1.542 (13)	C(14)—C(13)	1.540 (11)
C(18)—C(13)	1.512 (10)	C(15)—C(14)	1.527 (12)
C(16)—C(15)	1.532 (12)	C(17)—C(16)	1.502 (12)
C(18)—C(17)	1.552 (11)		
N(4)—S—N(1)	164.8 (3)	C(6)—S—N(1)	82.7 (4)
C(6)—S—N(4)	82.2 (4)	C(1)—N(1)—S	113.3 (6)
C(13)—N(1)—S	122.3 (5)	C(13)—N(1)—C(1)	124.4 (8)
C(2)—N(2)—C(1)	124.4 (8)	C(6)—N(2)—C(1)	114.8 (7)
C(6)—N(2)—C(2)	120.8 (8)	C(5)—N(3)—C(4)	124.4 (7)
C(6)—N(3)—C(4)	121.0 (7)	C(6)—N(3)—C(5)	114.5 (7)
C(5)—N(4)—S	115.8 (6)	C(7)—N(4)—S	121.2 (5)
C(7)—N(4)—C(5)	123.0 (8)	N(1)—C(1)—Se(1)	127.0 (8)
N(2)—C(1)—Se(1)	121.5 (6)	N(2)—C(1)—N(1)	111.4 (8)
C(3)—C(4)—N(3)	108.7 (7)	C(3)—C(2)—N(2)	108.5 (7)
N(3)—C(5)—Se(2)	120.7 (6)	C(4)—C(3)—C(2)	115.9 (8)
N(4)—C(5)—N(3)	109.3 (8)	N(4)—C(5)—Se(2)	129.9 (7)
N(3)—C(6)—S	118.1 (6)	N(2)—C(6)—S	117.8 (7)
N(3)—C(6)—N(2)	124.1 (8)	C(8)—C(7)—N(4)	113.2 (7)
C(12)—C(7)—N(4)	107.7 (7)	C(12)—C(7)—C(8)	112.1 (8)
C(9)—C(8)—C(7)	110.7 (8)	C(10)—C(9)—C(8)	112.3 (9)
C(11)—C(10)—C(9)	110.5 (9)	C(12)—C(11)—C(10)	110.0 (9)
C(11)—C(12)—C(7)	109.3 (8)	C(14)—C(13)—N(1)	109.9 (7)
C(18)—C(13)—N(1)	112.0 (7)	C(18)—C(13)—C(14)	111.9 (7)
C(15)—C(14)—C(13)	109.9 (8)	C(16)—C(15)—C(14)	112.5 (8)
C(17)—C(16)—C(15)	112.2 (8)	C(18)—C(17)—C(16)	112.2 (8)

selenium and carbon) and the estimated length of a carbon–selenium double bond (1.74 Å; Pauling, 1960). This indicates that the C=Se groups are conjugated with neighbouring N atoms. These C=Se bonds are slightly shorter than the C=Se bond in tetramethylselenourea [1.863 (4) Å; Foss & Maartmann-Moe, 1987]. The N(1)—C(1) and N(4)—C(5) bonds [1.324 (9) and 1.307 (10) Å] are much shorter than the N(2)—C(1) and N(3)—C(5) bonds which are 1.375 (11) and 1.414 (10) Å, respectively. This considerable difference in these pairs of N—C bond lengths indicates that the C(1)=Se(1) group is strongly conjugated with N(1) but to a much smaller extent with N(2) and that the C(5)=Se(2) group is likewise strongly conjugated with N(4) but not with N(3).

The C(6)—S bond length of 1.726 (8) Å is intermediate between that of a C—S single bond (1.82 Å) and that of a C=S double bond in thioureas (1.67 Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). Also the lengths of the N(2)—C(6) and the N(3)—C(6) bonds [1.345 (10) and 1.352 (10) Å, respectively] lie between that of an N—C single bond (1.48 Å) and that of an N=C double bond (1.28 Å), and are close to the N—C bond length (1.34 Å) in thioureas (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). This indicates that N(2) and N(3) are conjugated with the C(6)=S unit to a substantial degree. The title compound thus contains three islands of conjugation, namely the N(1)—C(1)—Se(1) unit, the N(4)—C(5)—Se(2) unit and the N(2)N(3)—C(6)—S unit. The molecule can therefore be represented approximately by (6).
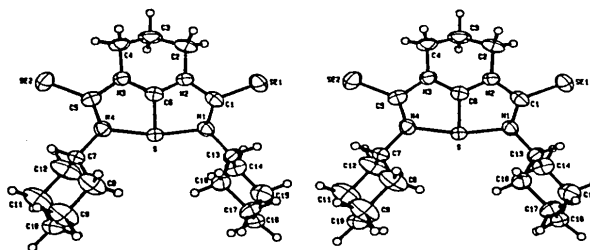

Fig. 1. Stereoscopic drawing to show molecular conformation and atomic numbering.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Birknes, B. & Hordvik, A. (1982). *Acta Chem. Scand. Ser. A*, 36, 813–818.

Foss, O. & Maartmann-Moe, K. (1987). *Acta Chem. Scand. Ser. A*, 41, 121–129.

Goerdeler, J. & Löbach, W. (1979). *Chem. Ber.* 112, 517–531.

Hordvik, A. & Julshamn, K. (1972). *Acta Chem. Scand.* 26, 343–354.

Iwasaki, F. & Akiba, K. (1981). *Acta Cryst.* B37, 180–185.

Iwasaki, F. & Akiba, K. (1984). *Bull. Chem. Soc. Jpn*, 57, 2581–2583.

Lai, L.-L. (1990). MSc Thesis, Univ. of the Witwatersrand, South Africa.

Matsumura, N., Tomura, M., Toriumi, K. & Yoneda, S. (1986). *Chem. Lett.* pp. 1047–1050.

MITCHELL, J. A. & REID, D. H. (1982). *J. Chem. Soc. Perkin Trans.* 1, pp. 499–507.

NICOL, R. H. (1983). PhD Thesis, Univ. of St. Andrews, Scotland.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

RHODES, J. B. (1987). PhD Thesis, Univ. of St. Andrews, Scotland.

SHELDRICK, G. M. (1978). In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.

Structure of Photochromic Spiroxazines. I. 1,3,3-Trimethylspiro[indoline-2,3'-[3H]-naphtho[2,1-b][1,4]oxazine]

BY ROBERTO MILLINI* AND GASTONE DEL PIERO

Eniricerche SpA, Via F. Maritano 26, I-20097 San Donato Milanese, Milano, Italy

PIETRO ALLEGRINI AND LUCIANA CRISCI

Enichem Synthesis, Via F. Maritano 26, I-20097 San Donato Milanese, Milano, Italy

AND VINCENZO MALATESTA

Istituto G. Donegani, Via G. Fauser 4, I-28100 Novara, Italy

Abstract. $C_{22}H_{20}N_2O$, $M_r = 328.4$, orthorhombic, *Pbca*, $a = 17.120$ (3), $b = 16.818$ (3), $c = 12.405$ (2) Å, $V = 3571.7$ (11) Å^3, $Z = 8$, $D_x = 1.221$ Mg m^{-3}, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 0.558$ mm^{-1}, $F(000) = 1392$, $T = 295$ K, $R = 0.053$ for 1762 reflections with $F > 2\sigma(F)$. The molecular structure consists of an indoline ring linked to a naphthoxazine ring through a spiro C atom. No significant distortion from the tetrahedral coordination was detected for the spiro C atom. All intermolecular distances agree with normal van der Waals interactions.

Introduction. Spiroindolinonaphthoxazines (I) exhibit photochromism and have higher durability with respect to photo-excitation than spiroindolinobenzopyrans. The better fatigue resistance renders this class of compounds most interesting for practical applications such as optical switches, filters, coatings for lenses and windows, optical memories *etc.*

The photochemical ring opening which results in the formation of red-absorbing merocyanine-like structures (II) has been extensively studied by ultrafast transient absorption and emission spectroscopy

(I)   (II)
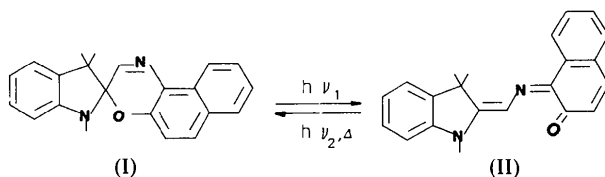
(Schneider, Mindl, Elfinger & Melzig, 1987; Schneider, Baumann, Klüter & Melzig, 1987; Kelmann, Tfibel, Dubest, Levoir, Aubard, Poitier & Guglielmetti, 1989; Bohne, Fan, Li, Lusztyk & Scaiano, 1990), nanosecond time-resolved spontaneous and coherent anti-Stokes Raman scattering (Albert, Bertigny, Aubard, Dubest & Dubois, 1985) and picosecond time-resolved resonance Raman spectroscopy (Aramaki & Atkinson, 1990). There is now a general consensus on the involvement of the excited singlet state S_1 in the cleavage of the C_{spiro}—O bond (Aramaki & Atkinson, 1990; Kelmann *et al.*, 1989; Schneider, Baumann *et al.*, 1987; Schneider, Mindl *et al.* 1987) with the only exception, in the class of spiropyran, for nitro-substituted indoline derivatives, for which the reactive state is T_1 (Sakuragi, Aoki, Tamaki & Ichimura, 1990). It was found that in the class of indoline spiropyrans the C_{spiro}—O bond is longer than the corresponding bond in the six-membered heterocycles (Aldoshin & Atovmyan, 1985). This may indicate an effective n_N-σ^* interaction between the indole nitrogen lone pair and a pyran C—O antibonding orbital in the ground state. The strength of this electronic interaction may be magnified in the excited state, providing the driving force for the photoinduced coloration reaction.

We have undertaken an extensive study of the molecular properties (photochromic activity, fatigue resistance *etc.*) of spirobenzoxazines, with the aim of evidencing structure–performance relationships