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Propellanes LXXIX.* Comparison of the Geometries of Dithia[*n*.3.3]propellanes (*n* = 1, 2, 3) and Dithia(and Oxathia)[4.3.3]propellenes. Study of the Influence of Complexation with $HgCl_2$, I_2, $CdCl_2$ and $PdCl_2$ and of Formation of Sulfoxides on some of these Compounds. Demonstration of the 'Klammer' Effect. Structures of Eighteen Crystals

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Abstract

The room-temperature crystal structures of eighteen compounds are reported. There are twelve molecular structures: dithia[3.3.1]propellane [$C_7H_{10}S_2$, *Cc*, $a = 6{\cdot}626\,(3)$, $b = 41{\cdot}077\,(20)$, $c = 6{\cdot}600\,(3)$ Å, $\beta = 120{\cdot}11\,(5)°$, $Z = 8$, $R_F = 0{\cdot}057$ for 1164 reflections], dithia[3.3.3]propellane [$C_9H_{14}S_2$, $P2_1/n$, $a = 11{\cdot}462\,(5)$, $b = 11{\cdot}428\,(5)$, $c = 7{\cdot}313\,(4)$ Å, $\beta = 95{\cdot}68\,(5)°$, $Z = 4$, $R_F = 0{\cdot}069$ for 1363 reflections] and dithia[4.3.3]propellene [$C_{10}H_{14}S_2$, $P2_1/c$, $a = 6{\cdot}897\,(4)$, $b = 23{\cdot}063\,(11)$, $c = 12{\cdot}656\,(6)$ Å, $\beta = 91{\cdot}29\,(5)°$, $Z = 8$, $R_F = 0{\cdot}069$ for 2043 reflections]; the isostructural centrosymmetric dimers of dithia[3.3.3]propellane.$HgCl_2$ [$C_9H_{14}S_2.HgCl_2$, $P2_1/c$, $a = 14{\cdot}320\,(6)$, $b = 9{\cdot}762\,(4)$, $c = 9{\cdot}058\,(4)$ Å, $\beta = 90{\cdot}32\,(5)°$, $Z = 4$, $R_F = 0{\cdot}081$ for 1927 reflections] and oxathia[4.3.3]propellene.$HgCl_2$ [$C_{10}H_{14}OS.HgCl_2$, $P2_1/c$, $a = 14{\cdot}926\,(6)$, $b = 9{\cdot}417\,(4)$, $c = 8{\cdot}744\,(4)$ Å, $\beta = 94{\cdot}77\,(5)°$, $Z = 4$, $R_F = 0{\cdot}065$ for 1907 reflections]; dithia[3.3.1]propellane.$2I_2$ [$C_7H_{10}S_2.2I_2$, $P\bar{1}$, $a = 11{\cdot}708\,(4)$, $b = 9{\cdot}491\,(3)$, $c = 7{\cdot}887\,(3)$ Å, $\alpha = 66{\cdot}03\,(5)$, $\beta = 104{\cdot}48\,(5)$, $\gamma = 110{\cdot}45\,(5)°$, $Z = 2$, $R_F = 0{\cdot}064$ for 2337 reflections] and dithia[3.3.2]propellane.$2I_2$ [$C_8H_{12}S_2.2I_2$, $P2_1/c$, $a = 8{\cdot}428\,(3)$, $b = 21{\cdot}839\,(7)$, $c = 9{\cdot}548\,(3)$ Å, $\beta = 115{\cdot}51\,(5)°$, $Z = 4$, $R_F = 0{\cdot}042$ for 2451 reflections]; dithia[3.3.3]propellane.$PdCl_2$ [$C_9H_{14}S_2.PdCl_2$, *Pmna*, $a = 13{\cdot}515\,(5)$, $b = 7{\cdot}412\,(4)$, $c = 11{\cdot}801\,(5)$ Å, $Z = 4$, $R_F = 0{\cdot}045$ for 1025 reflections]; dithia[4.3.3]propellene.$PdCl_2$ [$C_{10}H_{14}S_2.PdCl_2$, *Pnma*, $a = 14{\cdot}362\,(5)$, $b = 7{\cdot}422\,(4)$, $c = 11{\cdot}891\,(5)$ Å, $Z = 4$, $R_F = 0{\cdot}042$ for 994 reflections]; bis{oxathia[4.3.3]propellene}.$PdCl_2$ [$2C_{10}H_{14}OS.PdCl_2$, *Pbca*, $a =$

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* Part LXXVIII: Weinberg, Knowles & Ginsburg (1985).

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11·324 (5), $b = 11{\cdot}653$ (5), $c = 16{\cdot}233$ (6) Å, $Z = 4$, $R_F = 0{\cdot}051$ for 1378 reflections]; dithia[3.3.1]-propellane disulfoxide [$C_7H_{10}O_2S_2$, *Cmca*, $a =$ 8·160 (3), $b = 12{\cdot}965$ (4), $c = 15{\cdot}302$ (5) Å, $Z = 8$, $R_F = 0{\cdot}085$ for 735 reflections]; dithia[4.3.3]-propellene disulfoxide [$C_{10}H_{14}O_2S_2$, $P2_12_12_1$, $a =$ 13·160 (7), $b = 10{\cdot}674$ (5), $c = 7{\cdot}629$ (4), $Z = 4$, $R_F =$ 0·048 for 1024 reflections]. There are four polymeric structures: dithia[3.3.1]propellane.$HgCl_2$ [$C_7H_{10}S_2.HgCl_2$, *Pmmn*, $a = 12{\cdot}446$ (5), $b = 8{\cdot}680$ (4), $c = 5{\cdot}000$ (3) Å, $Z = 2$, $R_F = 0{\cdot}041$ for 522 reflections]; dithia[4.3.3]propellene.$HgCl_2$ [$C_{10}H_{14}S_2.HgCl_2$, $P\bar{1}$, $a = 11{\cdot}765$ (5), $b = 8{\cdot}701$ (4), $c = 7{\cdot}552$ (4) Å, $\alpha =$ 115·33 (5), $\beta = 103{\cdot}97$ (5), $\gamma = 83{\cdot}18$ (5)°, $Z = 2$, $R_F =$ 0·048 for 2164 reflections]; bis(dithia[4.3.3]-propellene).$CdCl_2$ [$2C_{10}H_{14}S_2.CdCl_2$, $P2_1/c$, $a =$ 6·968 (3), $b = 27{\cdot}428$ (12), $c = 12{\cdot}007$ (5) Å, $\beta =$ 97·67 (4)°, $Z = 4$, $R_F = 0{\cdot}058$ for 3021 reflections]; dithia[4.3.3]propellene disulfoxide monohydrate [$C_{10}H_{14}O_2S_2.H_2O$, *Pna*2_1, $a = 10{\cdot}685$ (5), $b =$ 10·100 (5), $c = 10{\cdot}591$ (5) Å, $Z = 4$, $R_F = 0{\cdot}050$ for 978 reflections]. There are two salts: {bis(dithia[3.3.2]propellane)palladium(II)}$Cl_2.4H_2O$ {[$Pd(C_8H_{12}S_2)_2$] $Cl_2.4H_2O$, $P2_1/c$, $a = 7{\cdot}256$ (4), $b = 9{\cdot}208$ (4), $c = 17{\cdot}208$ (8) Å, $\beta = 99{\cdot}78$ (5)°, $Z = 2$, $R_F = 0{\cdot}031$ for 1831 reflections} and {bis(dithia[3.3.3]propellane)palladium(II)}$Cl_2.4H_2O$ {[$Pd(C_9H_{14}S_2)_2$] $Cl_2.4H_2O$, $P\bar{1}$, $a = 9{\cdot}985$ (4), $b = 8{\cdot}772$ (4), $c = 7{\cdot}280$ (4) Å, $\alpha = 95{\cdot}09$ (4), $\beta = 98{\cdot}12$ (5), $\gamma = 78{\cdot}00$ (5)°, $Z = 1$, $R_F = 0{\cdot}036$ for 1987 reflections}. The structures of the molecular complexes can be related to those of known types except for the pairing found in I_2.dithia[3.3.1]propellane.I_2–I_2.dithia[3.3.1]propellane.I_2 and the six-coordinate polymeric arrangement in dithia[3.3.1]-propellane.$HgCl_2$. The two salts contain stepped ribbons of composition $(H_2O)_4(Cl^-)_2$ made up of linked six-membered ($4H_2O + 2Cl^-$) and four-membered ($2H_2O + 2Cl^-$) rings. Such an arrangement does not appear to have been reported previously. The propellane(ene) moieties have either an eclipsed or a staggered conformation about the conjoining bond. The dithia[*n*.3.3]propellanes with $n = 1, 2, 3$ are eclipsed and all three rings have C_s (m) conformations. Those dithia[4.3.3]propellenes with an eclipsed conformation have the three rings in the C_s (m) conformation while the rings in the staggered molecules have C_2 (2) symmetry. There are only three exceptions to this non-mixing rule among thirty-odd of the many propellane structures reported in the literature. The considerable deviations found from ideal conformations are ascribed to crystal packing effects and, for molecules with $n = 1$ and 2, to the deviations from tetrahedrality at the bridgehead atoms; this serves to explain the 'Klammer' effect. The lowest-energy conformations from molecular-mechanics calculations are generally those found experimentally.

I. Introduction

Crystal structures of many propellanes (tricycloalkanes) have been reported (see Ginsburg, 1975, 1981 for summaries) but intercomparison of these isolated examples does not permit a systematic study of stereochemical effects in the propellane series. However, the availability of the dithia[*n*.3.3]propellanes ($n = 1, 2, 3$) and the dithia(and oxathia)-[4.3.3]propellenes* (Weinges, 1981; Sataty, Kapon, Kaftory & Ginsburg, 1982; see Fig. 1) now makes it possible to study the stereochemistry of this group in a systematic way. These compounds contain flexible rings and form sulfoxides and also various molecular compounds by interaction of the sulfur atoms of the thiolane rings with electrophilic moieties such as $HgCl_2$, I_2, $CdCl_2$ and $PdCl_2$. Thus a variety of geometries can be anticipated. We report here the crystal structures of three host molecules ($n = 1, 3, 4$), three molecular complexes with $HgCl_2$ ($n = 1, 3, 4$), one with $CdCl_2$ ($n = 4$), two with I_2 ($n = 1, 2$) and four with $PdCl_2$ ($n = 2, 3, 4$). We also report the crystal structures of the complexes of oxathia[4.3.3]propellene with $HgCl_2$ and $PdCl_2$, of dithia[3.3.1]propellane disulfoxide, and of two stereoisomers of dithia[4.3.3]-propellene disulfoxide, one as the neat crystal and the other as the monohydrate. There are eighteen crystal structures in all. This enables us to compare the stereochemistry of the propellane(ene) molecules in their neat crystals with that found in their molecular complexes. We further compare the stereochemistry of the individual rings present in these molecules with that found for analogous rings without the constraints of other conjoined groups. The crystallographic results also enable us to investigate the 'Klammer'† effect, the prediction that the dihedral angle between the planes of the two thiolane rings will increase as n becomes smaller and so 'pinches' the thiolane rings

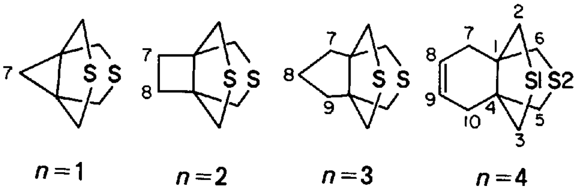

Fig. 1. Formulae of dithia[*n*.3.3]propellanes ($n = 1, 2, 3$) and dithia[4.3.3]propellene with the crystallographic numbering scheme used throughout the paper. Hydrogens are numbered for the carbons to which they are attached and distinguished as H(1)C(1), H(2)C(1) *etc.*

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* We shall refer to all four together, where possible, as dithia(or oxathia)[*n*.3.3]propellanes(enes) ($n = 1-4$); however, we follow standard practice in listing the ring sizes as [3.3.1], [3.3.2], [3.3.3] and [4.3.3].

† We cannot find the reference for this term but it is not our original idea; it may stem from a conversation with Professor H.-D. Martin [*cf.* 'Propellan-effekt' (Martin & Hekman, 1974)]. Some of our results have been briefly reported (Ashkenazi, Ginsburg, Kaftory, Kapon & Sataty, 1982).

apart. We have carried out a series of molecular-mechanics calculations [using Quantum Chemistry Program Exchange (QPCE) No. 395 (*MM*2)] on the propellane(ene) moieties in the various possible conformations in order to compare the order of calculated steric energies with the experimental conformations. The agreement is generally good.

II. Syntheses

The dithia[*n*.3.3]propellanes ($n = 1, 2, 3$) (see Fig. 1) were supplied by Weinges (1981), while dithia[4.3.3]-propellene (Altman, Babad, Pucknat, Reshef & Ginsburg, 1968) and oxathia[4.3.3]propellene (Ashkenazi, Oliker & Ginsburg, 1978) were prepared here. Preparation of 1:1 complexes of dithia[4.3.3]-propellene with $HgCl_2$ (Sataty, Kapon, Kaftory & Ginsburg, 1982) and $PdCl_2$, and the 2:1 complex with $CdCl_2$ has been reported (Sataty, Peled & Ginsburg, 1982). The complex of oxathia[4.3.3]propellene with $PdCl_2$ was reported as 3:2 (Sataty, Peled & Ginsburg, 1982) but the crystallographic results below show that it is 2:1.

The Pd complexes of dithiapropellanes(enes) were prepared by adding an aqueous solution of a Pd salt (K_2PdCl_4, K_2PdCl_6, $PdCl_2$) to an aqueous solution of the propellane(ene) at room temperature. The complex precipitated. Details of chemical analyses and IR spectra have been deposited.* The iodine complexes were prepared by mixing chloroform solutions of dithiapropellanes(enes) (10 mmol in 10 ml $CHCl_3$) and I_2 (0·8 mmol in 10 ml $CHCl_3$) and allowing them to stand.

Syntheses of the sulfoxides have been described (Sataty, Peled & Ginsburg, 1982). Satisfactory chemical analyses were obtained for all the compounds discussed.

III. Crystallographic studies and results

Similar methods were used in all the studies. After preliminary photography, cell dimensions were measured on a Philips PW1100/20 four-circle diffractometer, the space groups determined and intensities measured by standard techniques. Three standard reflections for each compound. Crystal data and essential experimental details are summarized in Table 1 while more extensive experimental details have been deposited.* Structures were determined by use of *SHELX*77 (Sheldrick, 1977) or MULTAN (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and refined using *SHELX*77. Anisotropic temperature factors were used for non-hydrogen atoms and isotropic temperature factors for hydrogens. Hydrogen parameters have been deposited, even if refined. We used the program *RING* (QCPE No. 228; Cremer, 1979) for the final geometrical calculations, including those of torsion angles and ring puckering parameters, from the atomic coordinates. (For convenience the atomic coordinates have been placed at the end of the paper, Table 12.) Details are discussed in § IV(1)(iv) and results are in Figs. 26-32. Comments in this section are restricted to special or unusual features; many data have been deposited (see deposition footnote).

(i) *Dithia*[3.3.1]*propellane.* The material sublimes so a crystal was sealed into a capillary. Although the cell dimensions suggest a metrically hexagonal cell, the diffraction patterns* and atomic coordinates are compatible only with a monoclinic cell, space group *Cc*. The two independent molecules in the asymmetric unit, which are closely similar and have approximate molecular symmetry C_{2v} (*mm*2), are not related by any symmetry element. The somewhat high correlation coefficients were ascribed to the obliquity of β. Atomic parameters are in Table 12(i) and a stereodiagram (Johnson, 1965) is in Fig. 2 (deposited).

(ii) *Dithia*[3.3.2]*propellane.* This structure could not be solved because the crystals were plastic and diffracted very poorly.

(iii) *Dithia*[3.3.3]*propellane* [*Table* 12(ii), *Fig.* 3 (*deposited*)]. The molecules have a propeller conformation.

(iv) *Dithia*[4.3.3]*propellene* [*Table* 12(iii); *Fig.* 4]. There are two molecules in the asymmetric unit. Each molecule is disordered by superposition of one thiolane and the cyclohexene ring, the other thiolane ring being ordered. The final stages of the refinement were carried out without constraining the thiolane

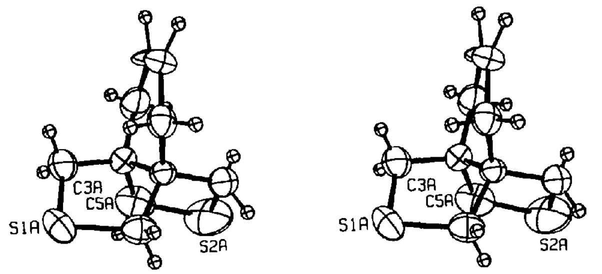

Fig. 4. Dithia[4.3.3]propellene - stereodiagram of the molecule based on refinement to $R = 0{\cdot}10$, *i.e.* before allowance was made for the positional disorder. One thiolane ring is ordered while there is superposition (disorder) of the other thiolane ring and the cyclohexene ring.

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* Lists of structure factors, anisotropic temperature factors, H-atom parameters, those diagrams mentioned in the text but not reproduced, the IUPAC names of the compounds and other material have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 42881 (204 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Merging, according to hexagonal symmetry, reflections that would be independent in a monoclinic cell, gave $R_{\rm int} = 20\%$, indicating that such merging was not justified.

Table 1. *Crystal data and*

	Dithia-[3.3.1]-propellane	Dithia-[3.3.3]-propellane	Dithia-[4.3.3]-propellene	Dithia-[3.3.1]-propellane.-$HgCl_2$	Dithia-[3.3.3]-propellane.-$HgCl_2$	Dithia-[4.3.3]-propellene.-$HgCl_2$	Oxathia-[4.3.3]-propellene.-$HgCl_2$	Bis(dithia-[4.3.3]-propellene).-$CdCl_2$	Dithia-[3.3.1]-propellane.-$2I_2$
	Transparent prisms	Transparent plates	Large transparent plates	Transparent prisms	Transparent prisms	Large transparent prisms	Large transparent plates	Large transparent laths	Deep-red prisms
Chemical formula	$C_7H_{10}S_2$	$C_9H_{14}S_2$	$C_{10}H_{14}S_2$	$C_7H_{10}S_2.HgCl_2$	$C_9H_{14}S_2.HgCl_2$	$C_{10}H_{14}S_2.HgCl_2$	$C_{10}H_{14}OS.HgCl_2$	$2C_{10}H_{14}S_2.CdCl_2$	$C_7H_{10}S_2.2I_2$
M_r	158·2	186·2	198·3	429·7	457·7	469·8	453·7	579·9	665·9
$F(000)$	672	400	848	396	856	440	848	1176	592
a (Å)	6·626 (3)	11·462 (5)	6·897 (4)	12·446 (5)	14·320 (6)	11·765 (5)	14·926 (6)	6·968 (3)	11·708 (4)
b (Å)	41·077 (20)	11·428 (5)	23·063 (11)	8·680 (4)	9·762 (4)	8·701 (4)	9·417 (4)	27·428 (12)	9·491 (3)
c (Å)	6·600 (3)	7·313 (4)	12·656 (6)	5·000 (3)	9·058 (4)	7·552 (4)	8·744 (4)	12·007 (5)	7·887 (3)
α (°)	—	—	—	—	—	115·33 (5)	—	—	66·03 (5)
β (°)	120·11 (5)	95·68 (5)	91·29 (5)	—	90·32 (5)	103·97 (5)	94·77 (5)	97·67 (4)	104·48 (5)
γ (°)	—	—	—	—	—	83·18 (5)	—	—	110·45 (5)
V (Å^3)	1554·0	953·2	2012·6	540·2	1266·2	678	1224·8	2274·2	744·4
D_m (g cm^{-3})	—	—	—	—	—	—	—	1·70	2·95
D_x (g cm^{-3})	1·350	1·298	1·309	2·643	2·402	2·302	2·461	1·694	2·972
Z	8	4	8	2	4	2	4	4	2
Space group	*Cc*	$P2_1/n$	$P2_1/c$	*Pmmn*	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
μ (cm^{-1})$^{(a)}$	52·0	43·3	41·3	153·5	130·9	122·3	133·9	15·5	86·4
Radiation$^{(b)}$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections in last refinement cycle	1164	1363	2043	522	1927	2164	1907	3021	2337
Criterion for omitted reflections$^{(c)}$	0	1·0	1·5	0	2·0	1·5	1·5	0	1·5
No. of parameters refined	241	156	231	47	127	136	136	244	158
Weighting$^{(d)}$ scheme $a =$	0·603	1·0	1·0	1·0	1·447	1·817	0·901	0·354	1·0
$b =$	0·0027	0·011	0·0097	0·0097	0	0·0013	0·0097	0·0009	0·0157
$R_F$$^{(e)}$	0·057	0·069	0·069	0·041	0·081	0·048	0·065	0·058	0·064
wR	0·062	0·081	0·063	0·049	0·074	0·049	0·075	0·049	0·079
$(\Delta/\sigma)_{\max}$$^{(f)}$	0·7	0·9	1·6	0·5	0·4	0·4	2·1	0·3	1·2
$(\Delta\rho)_{\max}$ (e Å^{-3})	0·3	0·7	0·4	1·5	4·1	2·5	2·6	0·6	2·1
$(\Delta\rho)_{\min}$ (e Å^{-3})	−0·4	−0·5	−0·3	−2·0	−4·8	−3·3	−2·6	−0·7	−3·5

Notes: (*a*) No absorption corrections were applied (*b*) When Cu $K\alpha$ was used, then $5° \leq 2\theta \leq 120°$; when Mo $K\alpha$ was used, then $5° \leq 2\theta \leq 50°$. (*c*) Given imposed by *SHELX*77). (*d*) The weighting scheme always had the form $w(F) = a/[\sigma^2(F_{obs}) + bF^2_{obs}]$. (*e*) R_F was greater than 0·07 in two refinements. dithia[3.3.1]propellane disulfoxide. (*f*) $(\Delta/\sigma)_{\max}$ values greater than unity were found for thermal parameters in some refinements, where limitations on

and cyclohexene rings. The occupation factors for sulfur and ethene groups were found to be 0·6/0·4 (molecule *A*) and 0·7/0·3 (molecule *B*); disordered ring dimensions were reasonable but appeared to suffer from minor systematic errors, probably because of high correlation factors, and so only some of the molecular dimensions are reported [Fig. 31(*a*)] and included in summaries and comparisons.

(v) *Dithia*[3.3.1]*propellane*.$HgCl_2$ [*Table* 12(iv); *Fig.* 5]. The Hg atom is at a site with *mm*2 symmetry; its *y* coordinate was found from a Patterson map. Further refinement (including hydrogens with isotropic temperature factors) was by standard methods. In this polymeric structure essentially unchanged $HgCl_2$ molecules are linked through S atoms of mirror-related dithia[3.3.1]propellane molecules and form sheets about (100).

(vi) *Dithia*[3.3.3]*propellane*.$HgCl_2$ [*Table* 12(v); *Fig.* 6, *cf. Fig.* 8]. The Hg atom was found from a Patterson synthesis. Further refinement was by standard methods. Hydrogens were introduced in calculated positions but not refined. The structural units in the crystal are centrosymmetric dimers in which the central four-membered rings have two Hg atoms bridged by two Cl's. The dimers, located at centres of symmetry at $\frac{1}{2}$, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, have the shapes of short cylinders, with the cylinder axes nearly along [100]. Packing of the layers of molecules in the *bc* plane is shown in Fig. 6.

(vii) *Dithia*[4.3.3]*propellene*.$HgCl_2$ [*Table* 12(vi); *Fig.* 7]. Although intensity statistics initially suggested that the space group was *P*1, refinement indicated that a centre of symmetry was present and the structure is reported in space group $P\bar{1}$. In this polymeric structure a modified $HgCl_2$ moiety bridges between S atoms of different dithia[4.3.3]propellene moieties.

(viii) *Oxathia*[4.3.3]*propellene*.$HgCl_2$ [*Table* 12(vii); *Fig.* 8]. The cell dimensions of this complex and of dithia[3.3.3]propellane.$HgCl_2$ are similar and the space groups are the same (Table 1); thus the two complexes are isostructural and the packing of the centrosymmetric moieties, which have very similar overall shapes despite the different organic ligands, is essentially that shown in Fig. 6.

(ix) *Bis*(*dithia*[4.3.3]*propellene*).$CdCl_2$ [*Table* 12(viii), *Fig.* 9]. This structure has a general resemblance to that of dithia[3.3.1]propellane.$HgCl_2$;

brief experimental details

Dithia[3.3.2]-propellane.-$2I_2$	Dithia[3.3.3]-propellane.-$PdCl_2$	Dithia[4.3.3]-propellene.-$PdCl_2$	[Bis(dithia-[3.3.2]-propellane).Pd]-$Cl_2.4H_2O$	[Bis(dithia-[3.3.3]-propellane.Pd]-$Cl_2.4H_2O$	Dithia[3.3.1]-propellane disulfoxide	Dithia[4.3.3]-propellene disulfoxide.-H_2O	Dithia[4.3.3]-propellene disulfoxide	Bis{oxathia-[4.3.3]-propellene}.-$PdCl_2$
Deep-red fragments	Orange needles	Fine yellow needles	Orange prisms	Large orange prisms	Transparent prisms	Transparent needles	Transparent plates	Deep-yellow prismatic needles
$C_8H_{12}S_2.2I_2$	$C_9H_{14}S_2.PdCl_2$	$C_{10}H_{14}S_2.$-$PdCl_2$	$[Pd(C_8H_{12}S_2)_2]$-$Cl_2.4H_2O$	$[Pd(C_9H_{14}S_2)_2]$-$Cl_2.4H_2O$	$C_7H_{10}O_2S_2$	$C_{10}H_{14}O_2S_2.$-H_2O	$C_{10}H_{14}O_2S_2$	$2C_{10}H_{14}OS.PdCl_2$
679·9	363·5	375·6	593·9	622·0	190·2	248·4	230·4	541·8
1216	720	744	608	320	800	528	488	1104
8·428 (3)	13·515 (5)	14·362 (5)	7·256 (4)	9·985 (4)	8·160 (3)	10·685 (5)	13·160 (7)	11·324 (5)
21·839 (7)	7·412 (4)	7·422 (4)	9·208 (4)	8·772 (4)	12·965 (4)	10·100 (5)	10·674 (5)	11·653 (5)
9·548 (3)	11·801 (5)	11·891 (5)	17·208 (8)	7·280 (4)	15·302 (5)	10·591 (5)	7·629 (4)	16·233 (6)
—	—	—	—	95·09 (4)	—	—	—	—
115·51 (5)	—	—	99·78 (5)	98·12 (5)	—	—	—	—
—	—	—	—	78·00 (5)	—	—	—	—
1586·1	1182	1267·5	1133·0	616·3	1618·9	1143·0	1071·6	2142·1
—	—	—	—	—	—	—	—	—
2·848	2·043	1·969	1·741	1·676	1·560	1·444	1·428	1·680
4	4	4	2	1	8	4	4	4
$P2_1/c$	*Pnma*	*Pnma*	$P2_1/c$	$P\bar{1}$	*Cmca*	$Pna2_1$	$P2_12_12_1$	*Pbca*
81·8	22·7	21·3	14·1	13·0	5·34	38·51	41·08	12·97
Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
2451	1025	994	1831	1987	735	978	1024	1378
1·5	1·5	1·5	1·5	1·5	0	0	0	1·5
175	103	104	188	205	85	199	183	180
1·701	1·249	0·917	1·038	0·902	0·368	1·0	1·0	1·502
0·00107	0·0017	0·0022	0·0004	0·0015	0·004	0·0215	0·011	0·004
0·042	0·045	0·042	0·031	0·036	0·085	0·050	0·048	0·051
0·048	0·054	0·046	0·033	0·038	0·080	0·052	0·049	0·047
1·6	0·7	0·1	0·3	1·2	0·7	0·8	0·3	0·6
1·0	0·8	0·7	0·4	0·7	0·7	0·3	0·3	0·5
−1·0	−1·4	−0·7	−1·5	−1·2	−0·6	−0·6	−1·9	−0·6

as k where the criterion is reflections omitted when $F_{obs} \leq k\sigma(F_{obs})$. Thus $k = 0$ means that all reflections were included except for $F_{obs} = 0$ (limitation This is ascribed to omission of absorption corrections for dithia[3.3.3]propellane.$HgCl_2$ and incomplete allowance for disorder (of an oxygen) in available computer time prevented attainment of complete convergence.

there are, however, some important differences. One S atom of each propellene ligand is linked to Cd in the present compound, whereas in the $HgCl_2$ complex both S atoms of the propellane bridge between (different) Hg atoms. Thus there is a polymeric *ribbon* structure in the $CdCl_2$ complex but a polymeric *sheet* structure in the $HgCl_2$ complex.

(x) *Dithia*[3.3.1]*propellane*.$2I_2$ [*Table* 12(ix), *Fig.* 10]. This is a molecular structure where an iodine molecule is linked to each sulfur of a given dithia[3.3.1] propellane molecule by a charge-transfer bond, with the additional unusual feature that two such units are linked by an I···I interaction [$d(I\cdots I) =$ 3·720 (1) Å, see Fig. 10].

(xi) *Dithia*[3.3.2]*propellane*.$2I_2$ [*Table* 12(x); *Figs.* 11 (*deposited*) *and* 12]. The molecular structure (Fig. 11) is similar to that of the [3.3.1] analogue; however, the overall arrangement (Fig. 12) shows that there are no close $I_2\cdots I_2$ interactions.

(xii) *Dithia*[3.3.3]*propellane*.$PdCl_2$ [*Table* 12(xi) *and Fig.* 13 (*deposited*)]. The Pd and Cl atoms were located from a Patterson map; refinement indicated that the space group was *Pnma* and not its noncentrosymmetric congener. This is a molecular structure in which the $PdCl_2$ group bridges between two S atoms of the same molecule. The molecule has (crystallographic) C_s (m) symmetry but does not attain C_{2v} ($mm2$) symmetry because of the envelope conformation of the C_5 ring.

(xiii) *Dithia*[4.3.3]*propellene*.$PdCl_2$ [*Table* 12(xii), *Fig.* 14 (*deposited*)]. This is a molecular structure analogous to that of dithia[3.3.3]propellane.$PdCl_2$ with similar bridging of S atoms by $PdCl_2$. The molecule has C_s (m) symmetry but does not attain $mm2$ symmetry because the C_6 ring has a boat conformation. Although the cell dimensions of dithia[3.3.3]-propellane.$PdCl_2$ and dithia[4.3.3]propellene.$PdCl_2$ are very similar, the space groups are the same and both molecules lie in mirror planes parallel to (010), nevertheless the two crystals are *not* isostructural. In dithia[3.3.3]propellane.$PdCl_2$ the vector that bisects the Cl–Pd–Cl angle is parallel to [001] whereas the analogous vector in dithia[4.3.3]propellene.$PdCl_2$ is parallel to [100].

(xiv) *Bis*(*oxathia*[4.3.3]*propellene*).$PdCl_2$ [*Table* 12(xiii), *Fig.* 15 (*deposited*)]. The Pd atom is at the origin; hydrogen positions and isotropic temperature factors were refined. This is a molecular structure in which two oxathia[4.3.3]propellene molecules are linked, *trans*, to Pd. The oxygen atoms do not participate in the bonding. The overall arrangement is analogous to that found in *trans*-dichlorobis-(sulfaguanidine)palladium(II) (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976).

(xv) {*Bis*(*dithia*[3.3.2]*propellane*)*palladium*(II)}-$Cl_2.4H_2O$ [*Table* 12(xiv), *Fig.* 16]. Unlike all the previous compounds, which were molecular or polymeric in nature, this material is a hydrated salt. All hydrogens, including those of the water molecules, were found and their positions and isotropic temperature factors refined. The cation is centrosymmetric with Pd^{2+} bridging four S atoms of two dithia[3.3.2]propellane molecules; its symmetry is nearly D_{2h} (*mmm*). Because of the bridging role of the Pd^{2+} ion, the

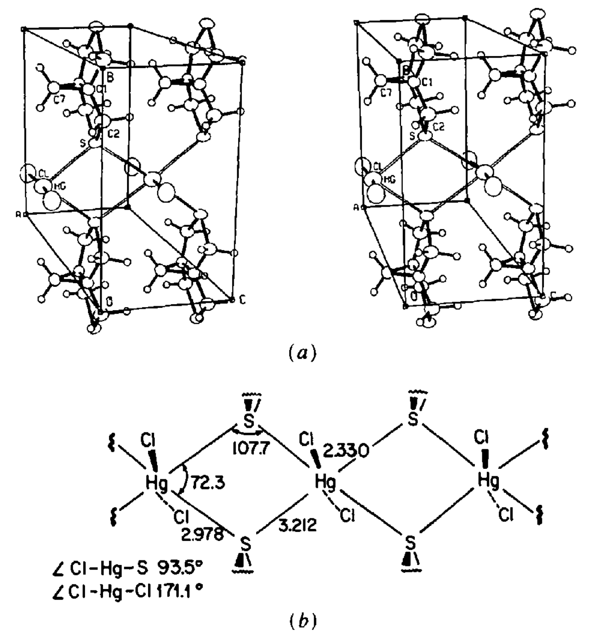


Fig. 5. Dithia[3.3.1]propellane.$HgCl_2$. (*a*) Stereodiagram of the unit cell showing the polymeric sheets lying about the (100) planes. (*b*) Schematic diagram of $S\cdots HgCl_2$ interactions. The Hg and S atoms lie in the (100) mirror plane, to which the Hg–Cl vectors are nearly normal. Only one S of each propellane moiety is shown but the second participates in a similar ribbon structure leading to the overall formation of a sheet structure.

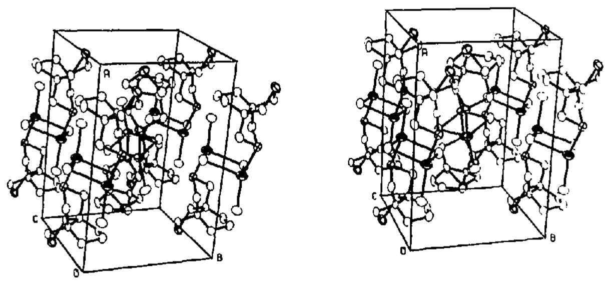


Fig. 6. Dithia[3.3.3]propellane.$HgCl_2$ - stereodiagram of the unit cell, showing the packing of the quasi-cylindrical structural units. The Hg and S atoms have been differentiated. See Fig. 8 for dimensions.

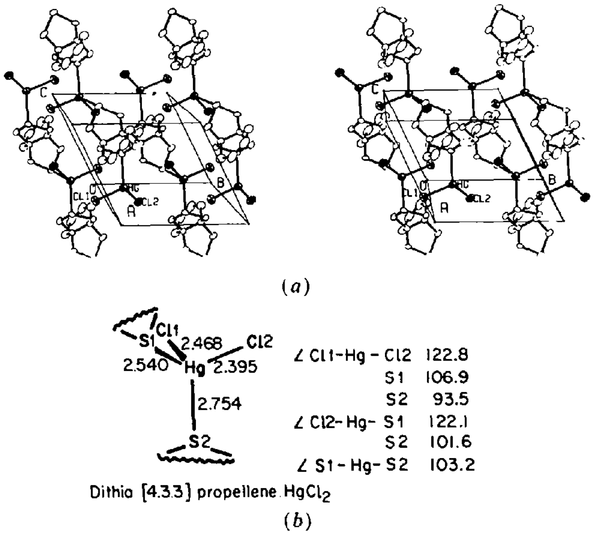


Fig. 7. Dithia[4.3.3]propellene.$HgCl_2$. (*a*) Stereodiagram of the unit cell. (*b*) Dimensions of the atomic arrangement about Hg. The e.s.d.'s of the bond lengths are ~0·005 Å and of the bond angles ~0·2°.

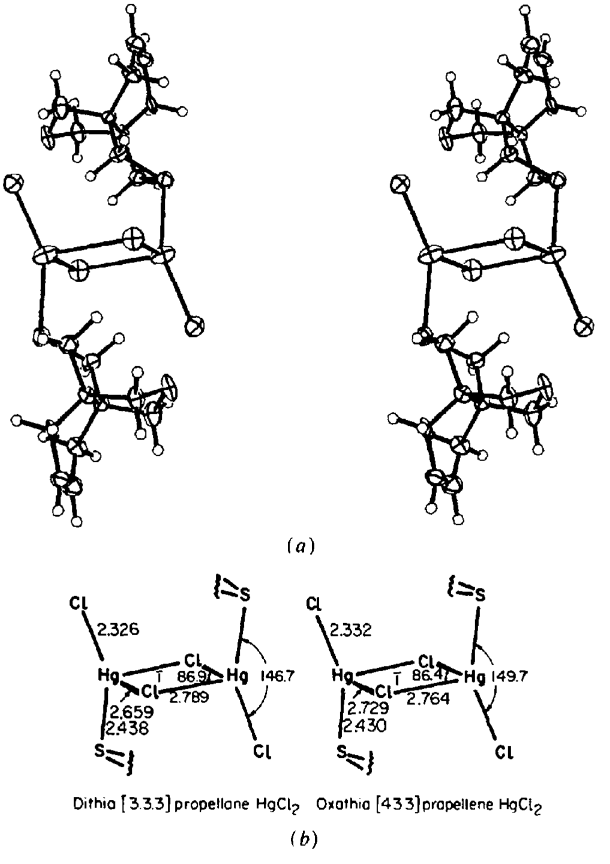
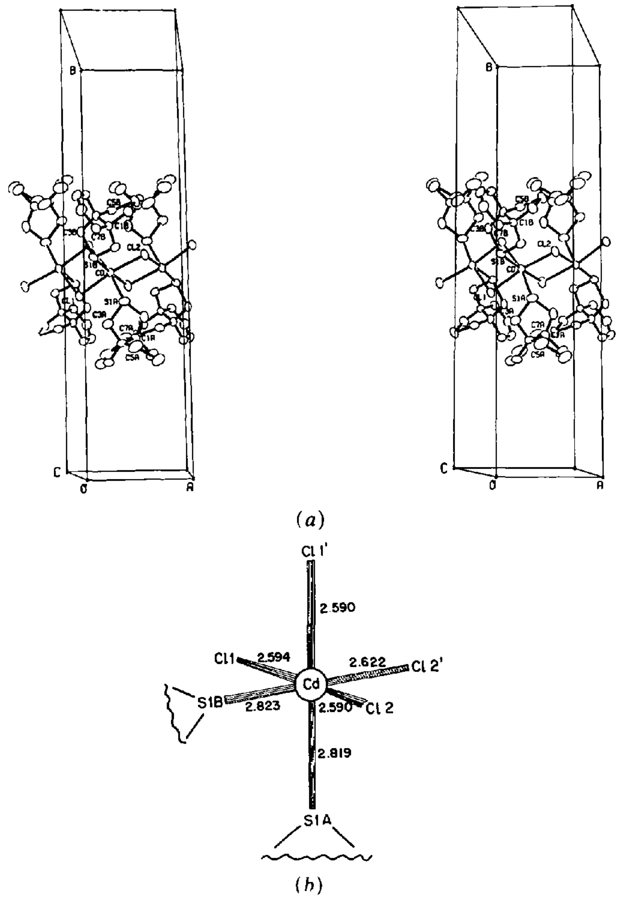


Fig. 8. Oxathia[4.3.3]propellene.$HgCl_2$. (*a*) Stereodiagram of the centrosymmetrical structural unit; for packing arrangement *cf.* Fig. 6. (*b*) Comparison of dimensions in the central regions of the two similarly shaped centrosymmetric dimers; the e.s.d.'s are similar to those given in the caption to Fig. 7. Note that bridging Cl is designated as Cl(1) [Table 12(v)] in dithia[3.3.3]propellane.$HgCl_2$ but as Cl(2) [Table 12(vii)] in oxathia[4.3.3]propellene.$HgCl_2$.

conformations of the thiolane rings and of the dithia[3.3.2]propellane moieties are very similar to those found in the dithia[*n*.3.3]propellane(ene).$PdCl_2$ ($n = 3, 4$) molecules. The Cl^- anions and the water molecules are arranged in puckered ribbons (Fig. 17) of linked six-membered ($2Cl^- + 4H_2O$) and four-membered ($2Cl^- + 2H_2O$) rings. These ribbons run in the [100] direction between the cations but are not linked to one another.

(xvi) {*Bis*(*dithia*[3.3.3]*propellane*)*palladium*(II)}-$Cl_2.4H_2O$ [*Table* 12(xv), *Fig.* 18 (*deposited*)]. This material is a hydrated salt, analogous to (xv). The cation structures are analogous; the cation symmetry is nearly C_{2h} ($2/m$), reduced from that in (xv) because of the envelope conformation of the C_5 ring as compared to the planarity of the C_4 ring. The arrangement of Cl^- ions and H_2O molecules is similar to that found in (xv). Crystals (xv) and (xvi) are monoclinic and triclinic packings of similar arrangements.



(*a*)

(*b*)

Fig. 9. Bis(dithia[4.3.3]propellene).$CdCl_2$. (*a*) Stereodiagram of the unit cell showing polymeric ribbons extending along [100]. (*b*) Geometrical details of coordination about Cd; S(1*A*) and S(1*B*) are sulfur atoms of the two independent propellene molecules in the asymmetric unit. The e.s.d.'s of the bond lengths are ~0·002 Å and of the bond angles ~0·1°. The bond angles about Cd are:

Cl(1)–Cd–Cl(1')	86·6°	Cl(1')–Cd–S(1*B*)	86·2°
Cl(1)–Cd–Cl(2')	94·9	Cl(2)–Cd–Cl(2')	82·1
Cl(1)–Cd–S(1*A*)	86·3	Cl(2)–Cd–S(1*A*)	85·1
Cl(1)–Cd–S(1*B*)	89·4	Cl(2)–Cd–S(1*B*)	93·4
Cl(1')–Cd–Cl(2)	103·0	Cl(2')–Cd–S(1*A*)	101·0
Cl(1')–Cd–Cl(2')	96·1	S(1*A*)–Cd–S(1*B*)	77·2.

Cl(1') and Cl(2') are at 56502 and 66502 respectively. These codes are according to *ORTEP* notation (Johnson, 1965). The sequence of symmetry elements is that given in *International Tables for X-ray Crystallography* (1952).

(xvii) *Dithia*[3.3.1]*propellane disulfoxide* [*Table* 12(xvi), *Fig.* 19 (*deposited*)]. The molecules are located at Wyckoff positions (*f*) of space group *Cmca*, *i.e.* across the mirror planes at $x = 0, \frac{1}{2}$. Anisotropic refinement of non-hydrogen atoms and isotropic refinement of hydrogens converged at $R = 0{\cdot}11$. A difference synthesis showed a peak of height ~2 e $Å^{-3}$ at 1·31 Å from S(1). This was attributed to the presence of a second stereoisomer with oxygen bonded equatorially to S(1). Refinement was continued with O(1) split into two occupancies, 80% (anisotropic temperature factors) and 20% (isotropic temperature factors) and converged at $R = 0{\cdot}085$. Thus this crystal is a molecular complex of two stereoisomers; presumably there is solid solution of the minor component in the major but this has not been proved. Another possibility is that the complex consists of 80% disulfoxide and 20% dithia[3.3.1]propellane *S*-dioxide *S'*-oxide but this is unlikely on chemical grounds. In what follows we shall consider this material to be a solid solution of the two stereoisomers.

(xviii) *Dithia*[4.3.3]*propellene disulfoxide* [*Table* 12(xvii), *Figs.* 20 *and* 21 (*deposited*)]. This is a molecular structure with the two sulfoxide groups *syn* to each other. The conformation assumed by the

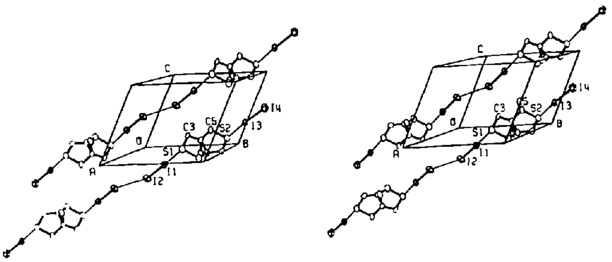


Fig. 10. Dithia[3.3.1]propellane.$2I_2$ - stereodiagram of the unit cell, showing the combination of two dithia[3.3.1]propellane.$2I_2$ units to form the paired packing unit.

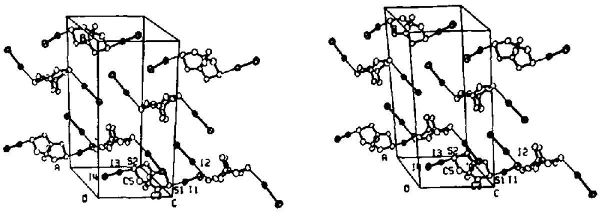


Fig. 12. Dithia[3.3.2]propellane.$2I_2$ - stereodiagram of the unit cell, showing that the packing unit is the single dithia[3.3.2]propellane.$2I_2$ unit. Note that the disposition of the I_2 molecules with respect to the propellane moiety is the same in both dithia[3.3.1]propellane.$2I_2$ and dithia[3.3.2]propellane.$2I_2$.

molecule in the crystal is chiral; as the space group ($P2_12_12_1$) is also chiral, spontaneous resolution has occurred on crystallization. The absolute configuration of the crystal used was not determined nor whether it was twinned.

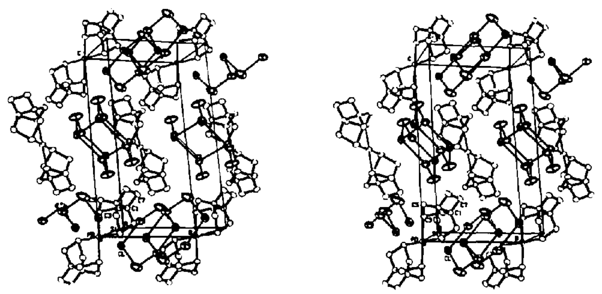


Fig. 16. [Bis(dithia[3.3.2]propellane)palladium(II)]$Cl_2.4H_2O$ - stereodiagram of the unit cell. Pd atoms are at centers of symmetry and linked to both S of each propellane moiety. A Cl atom of the ribbon is labeled.

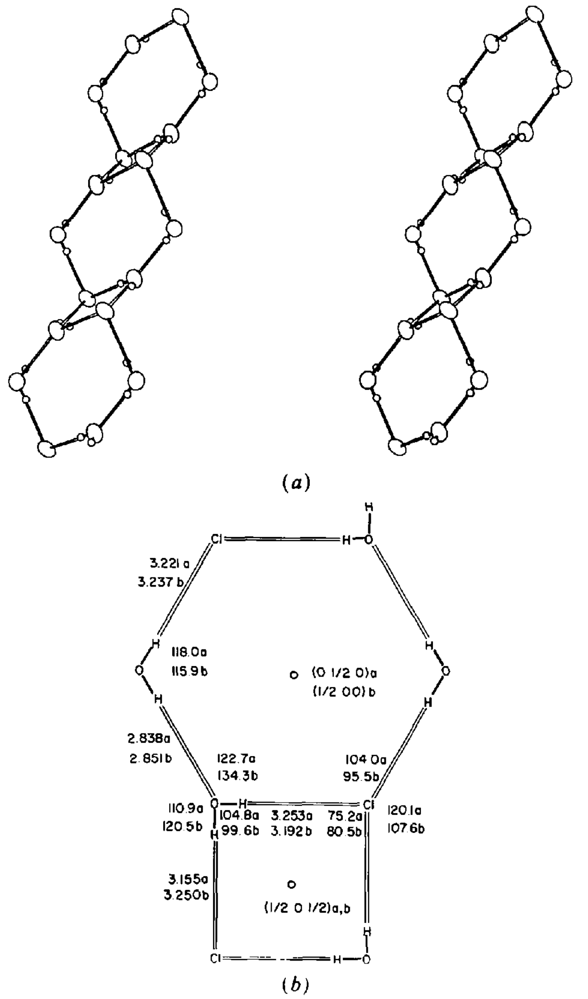


Fig. 17. [Bis(dithia[*n*.3.3]propellane)palladium(II)]$Cl_2.4H_2O$ ($n = 2, 3$). (*a*) Stereodiagram of the network formed by water molecules and Cl^- ions. (*b*) Geometrical details of the network formed by H_2O molecules and Cl^- ions - '*a*' denotes values for $n = 2$ and '*b*' for $n = 3$.

(xix) *Dithia*[4.3.3]*propellene disulfoxide monohydrate* [*Table* 12(xviii), *Figs.* 22 *and* 23]. In the propellane moiety the two sulfoxide groups are *anti* to each other. The structure is polymeric; helices with their axes along [100] are formed from adjacent propellene molecules which are hydrogen-bridged by water molecules linking their oxygen atoms; the hydrogen-bond distances are $d[OW \cdots O(1)] = 2{\cdot}83\,(1)$, $d[OW \cdots O(2)] = 2{\cdot}93\,(1)$ Å.

(xx) *Details of* Cl^--H_2O *networks.* The salts {bis(dithia[*n*.3.3]propellane)palladium(II)}$Cl_2.4H_2O$ ($n = 2$, Fig. 16; $n = 3$, Fig. 18) contain very similar ribbons of composition $(H_2O)_4(Cl^-)_2$ [stereodiagram in Fig. 17(*a*) and geometrical details in Fig. 17(*b*)]. Both six- and four-membered rings are centrosymmetric; the six-membered ring has a chair conformation and the four-membered ring is planar. The dimensions of the ribbons for $n = 2$ and 3 are similar but not identical; the hydrogen-bond lengths and angles fall within the usual range of values. The disposition of bonds at the oxygen linking the two rings is pyramidal for $n = 2$ [$\sum$(bond angles) = 338°]

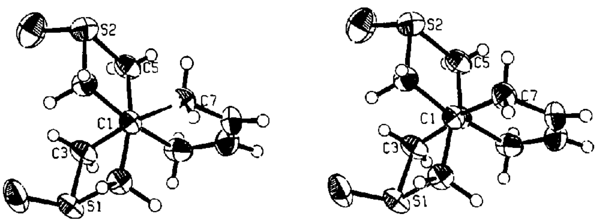


Fig. 20. Dithia[4.3.3]propellene disulfoxide - stereodiagram of the molecule.

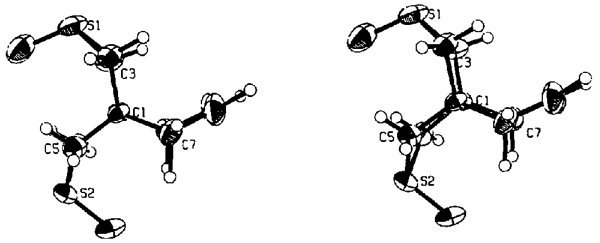


Fig. 22. Dithia[4.3.3]propellene disulfoxide monohydrate - stereodiagram of the propellene moiety.

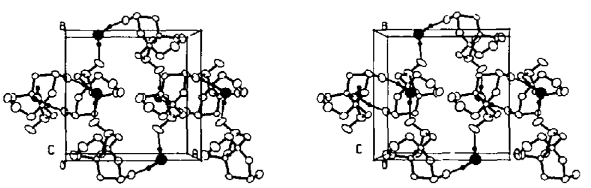


Fig. 23. Dithia[4.3.3]propellene disulfoxide monohydrate - stereodiagram of the unit cell. Both oxygens of sulfoxide groups are H-bonded to bicoordinate water molecules (darkened), forming spirals along [100].

and almost trigonal planar for $n=3$ ($\sum=354°$). At the Cl^- ions the disposition of bonds is distorted pyramidal with $\sum$ values of 299 and 284° respectively.

IV. Results and discussion

The structural aspects of the present group of compounds can be compared in a number of different, but interdependent, ways. Attention will first be directed to the geometries of the various ring systems in the dithia[*n*.3.3]propellane(ene) moieties and their analogues. With this as basis we next consider the modes of combination of these rings to give the propellane(ene) moieties, and the overall geometries and symmetries of these moieties. This is an appropriate place to consider the influence of the size of the aliphatic ring (*i.e.* the value of *n*) on the dithia[*n*.3.3]propellane(ene) geometry and leads to a discussion of the 'Klammer' effect. We then consider the various modes of complexation *via* the sulfur atoms and compare the present complexes with others of the same types. Finally the $Cl^- \cdots H_2O$ networks are discussed.

(1) *Conformations and dimensions of the rings of the dithia(and oxathia)[n.3.3]propellanes(enes) and related molecules*

(i) *Introduction and background.* We begin by reviewing the conformations assumed by small ring systems (Dunitz, 1979; Romers, Altona, Buys & Havinga, 1969; Bucourt, 1974; Fuchs, 1978). The 3-ring is necessarily planar. The regular 4-ring (equilateral, isogonal) can buckle, *i.e.* have non-zero torsion angles with concomitant changes in bond angle. The relation between torsion angle (τ) and bond angle (θ; angles in degrees) is (Dunitz, 1979):

$$\tau = 15{\cdot}1(\theta - 90)^2.$$

The puckered form of cyclobutane has been found to be more stable by 5·35 kJ mol^{-1} than the planar form (Ueda & Shimanouchi, 1968); the torsion angle is 25° and the bond angles are thus 88·7 and 91·3°. Similar values are quoted by Allen (1984*a*,*b*).

The *regular* 5-ring must be planar but can distort, with concomitant changes in bond lengths and/or bond angles (more probably the latter), to lower-energy conformations. These interconvert by a process known as pseudorotation, there being no potential barrier between the conformers in cyclopentane [see Dunitz (1979) and Strauss (1983) for summary and references]. Two particular conformers are usually singled out in cyclopentane (and by extension in other five-membered rings); these are the half-chair (or twist) form with C_2 (2) symmetry and the envelope form with C_s (m) symmetry. Nomenclature is given in Fig. 24 and the relations among the torsion angles are shown in Fig. 25(*a*). Tetrahydrofuran does not appear to have a preferred conformation in the gas phase and the energy difference between 2 and *m* conformations has been estimated as 0·0 ± 1·2 kJ mol^{-1} (Almenningen, Seip & Willadsen, 1969). The 2 conformation found in crystalline 3,3,4,4-tetrahydrofurantetrol (Mighell & Jacobson, 1964) was attributed to the need to minimize interaction between vicinal hydroxy groups. Calculations by Nahlovska, Nahlovsky & Seip (1969) for the thiolane ring indicate that the 2 conformation is more stable than the *m* form by 8 kJ mol^{-1}, while Allegra, Wilson, Benedetti, Pedone & Albert (1970) report 20 kJ mol^{-1} for this energy difference. Electron diffraction shows that thiolane has the 2 conformation in the gas phase (Nahlovska *et al.*, 1969). Although there is disorder in the crystals of the thiolane.Br_2 molecular compound, the structure has been interpreted in terms of a 2 conformation for the thiolane ring (Allegra *et al.*, 1970).

The lone pairs at S in the *m* conformation of thiolane are not equivalent and are designated '*axial*' and '*equatorial*' (Fig. 24). In the various propellane(ene) molecules the envelope flaps can be directed either antiparallel to the aliphatic ring ('*anti*'

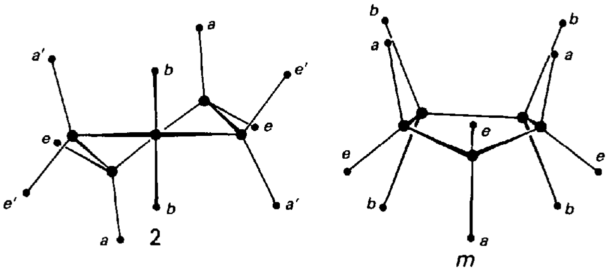


Fig. 24. Diagrams of the symmetrical conformations of the five-membered ring *m* (envelope) and 2 (twist or half-chair). The notation used for hydrogens and lone pairs is shown, assuming all atoms to be sp^3 hybridized (a = axial, e = equatorial, a' = pseudo-axial, e' = pseudo-equatorial, b = bisectional or isoclinal). In both diagrams the conjoining (propeller) bond of the propellane(ene) moiety faces the viewer; the CH_2 group opposite the conjoining bond is replaced by O in oxolane and by S in thiolane. Diagram modified from Eliel (1962).

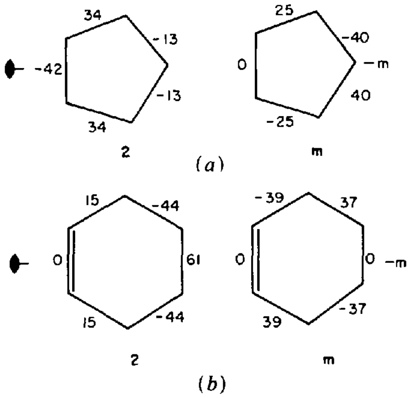


Fig. 25. Torsion angles ($\tau°$) for 2 and *m* conformations of cyclopentane rings; reversal of signs of τ gives mirror-image conformations; see also Fig. 24.

Table 2. *Conformations of thiolane rings in the compounds investigated*

The conformations are referred to as 2 and *m* for convenience, but there are generally significant deviations from these idealized situations.

2 conformation	*m* conformation
Dithia[4.3.3]propellene Dithia[4.3.3]propellene.$HgCl_2$	Dithia[3.3.1]propellane (both crystallographically independent moieties in the neat crystals)
Bis(dithia[4.3.3]propellene).$CdCl_2$ (both crystallographically independent moieties)	Dithia[3.3.1]propellane.$HgCl_2$ Dithia[3.3.1]propellane.$2I_2$ Dithia[3.3.1]propellane disulfoxide
Oxathia[4.3.3]propellene.$PdCl_2$	Dithia[3.3.2]propellane.$2I_2$ {(Dithia[3.3.2]propellane)$_2$palladium(II)}$Cl_2.4H_2O$
Dithia[4.3.3]propellene disulfoxide (in the neat crystals)	Dithia[3.3.3]propellane Dithia[3.3.3]propellane.$HgCl_2$ Dithia[3.3.3]propellane.$PdCl_2$ {(Dithia[3.3.3]propellane)$_2$palladium(II)}$Cl_2.4H_2O$
	Dithia[4.3.3]propellene.$PdCl_2$ Oxathia[4.3.3]propellene.$HgCl_2$ Dithia[4.3.3]propellene disulfoxide (in the monohydrate)

arrangement) or somewhat towards the aliphatic ring ('*syn*' arrangement). In the 2 conformation of thiolane the S lone pairs are equivalent and are called *bisectional* or *isoclinal* (Fig. 24). They can be distinguished in dithia(and oxathia)[4.3.3]propellene (and in the sulfoxides) because one lone pair of each S can be described as *anti* with respect to the mean plane of the cyclohexene ring, and the other as *syn*.

The half-chair form of the cyclohexene ring [as found in the vapor (Scharpen, Wollrab & Ames, 1968; Chiang & Bauer, 1969) and in crystalline 1-cyclohexenyl-1-cyclobutenedione (Karle, Britts & Brenner, 1964)] is the most stable conformation, with the 1,2-diplanar form 5·0 kJ mol^{-1} less stable, the 1,3-diplanar form (the screw-boat form) 20·1 kJ mol^{-1} and the 1,4-diplanar form (the boat form) 25·5 kJ mol^{-1} less stable (Bucourt, 1974). Torsion angles for the first and last of these conformations (the only ones found in the present study) are given in Fig. 25(*b*).

We now group together the dimensions and conformations of each type of propellane(ene) moiety (*i.e.* for each value of *n*) (Figs. 26-31; Tables 2-7) and discuss various aspects of these results.

(ii) *Dimensions of thiolane rings.* The results summarized in Table 2 show that only the *m* conformation of the thiolane ring appears in dithia[*n*.3.3]propellanes when $n = 1, 2, 3$. Thus, in these molecules, the steric requirements of the molecule as a whole outweigh those of the individual thiolane rings. In dithia[4.3.3]propellenes the 2 conformation of the thiolane rings appears about twice as often as the *m* conformation; the influence of the molecule as a whole is clearly less decisive.

The bond lengths do not vary significantly from one molecule to the next, irrespective of conformation, apart from the central C-C bond which is discussed below. The mean values* are

d(C–C) = 1·523 (17) Å [56 values]
d(C–S) = 1·818 (13) Å [48 values]
{d(C–O) = 1·428 (10) Å [4 values] for the tetrahydrofuran ring}.

In thiolane [electron diffraction, twist conformer (Nahlovska *et al.*, 1969)] d(C–C) = 1·536 (2) and d(C–S) = 1·839 (2) Å.

The bond angles (Figs. 26-31 and Table 3) are somewhat more variable than the bond lengths and there appear to be effects of both ring size and conformation on all the angles except for ∠SCC. As one might anticipate, the largest effects are for $n = 1$. Bond lengths and angles from the three sulfoxides have not been included in these averages but their values fit into the ranges found for the propellanes(enes). There are two tetrahydrofuran rings in the molecules investigated (both in $n = 4$ molecules); one has *m* and the other 2 symmetry. The mean value of ring bond angle is 104·3 (3·1)° [10 values]; there are too few results for effects of ring conformation to emerge.

The torsion angles (summary in Table 4, details in Figs. 26-31) provide a clear means of distinguishing between *m* and 2 conformations. Ideal *m* symmetry is found only when imposed crystallographically; otherwise there are appreciable deviations from the ideal values, which are discussed below [§ IV(1)(iv)].

(iii) *The aliphatic rings.* The results, averaged over the examples encountered here but excluding disordered structures, are summarized in Fig. 32.

The C_3 rings (five examples) are equilateral within the limits of error. The C–C bond distance is not significantly different from that found for 27 cyclopropane rings with only H or C(sp^3) substituents (Allen, 1980).

There are only two results for C_4 rings, which are both found to be planar. The ring shape is slightly

Table 3. *Summary of values of bond angles* (°) *found in thiolane rings of molecules of this study*

Results are given in the form: mean (population standard deviation) [number in sample]. The complete list of angle values has been deposited.

m conformation		
∠CSC	$n = 1$	94·3 (1·4) [7]
	2	91·0 (1·7) [4]
	3	89·0 (0·3) [8]
	4	87·7 (0·3) [3]
∠SCC	$n = 1$	107·1 (0·9) [13]
	2	106·0 (0·9) [7]
	3	106·8 (1·4) [16]
	4	106·1 (2·5) [4]
∠CCC	$n = 1$	113·2 (1·6) [13]
	2	109·7 (1·2) [8]
	3	107·9 (0·4) [16]
	4	108·5 (1·1) [4]

2 conformation ($n = 4$)	
∠CSC	93·7 (0·5) [7]
∠SCC	107·1 (0·9) [14]
∠CCC	106·2 (0·9) [14]

Thiolane by electron diffraction (Nahlovska *et al.*, 1969)	
∠CSC	93·4 (5)
∠SCC	106·1 (4)
∠CCC	105·0 (5)

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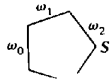
* The bracketed numbers are the ($N - 1$) sample standard deviations; this convention is used throughout this paper.

Table 4. *Mean values of torsion angles* (°) *found in the m and* 2 *conformations of the thiolane rings of the molecules included in this study* (*signs of torsion angles not taken into account in averaging*); *results are given in same form as for Table* 3



(1) *m* conformation

Torsion angle	Ideal C_5 ring	[3.3.1]	[3.3.2]	[3.3.3]	[4.3.3]
ω_0	0	0·8 (1·7) [7]	0·9 (1·2) [3]	−0·4 (0·6) [10]	−0·5 (1·9) [4]
ω_1	25	15·2 (3·8) [13]	27·2 (3·0) [8]	30·0 (1·3) [16]	30·0 (3·3) [6]
ω_2	−40	−20·8 (4·8) [13]	−37·9 (3·9) [8]	−41·8 (2·0) [16]	−43·4 (2·7) [6]

(2) 2 conformation

Torsion angle	Thiolane (electron diffraction) (Nahlovska *et al.*, 1969)	[4.3.3]
ω_0	−52·5 (1·6)	−47·2 (1·9) [9]
ω_1	40·5 (1·2)	36·5 (3·6) [18]
ω_2	−14·8 (0·5)	−13·4 (4·5) [18]

Table 5. *Puckering parameters for the cyclohexene rings in the propellanes of this study*

Compound	Q (Å)	φ (°)	θ (°)	Conformation following Boeyens (1978)*
(1) Dithia[4.3.3]propellene.-$PdCl_2$	0·670	60·0	90·0	$B_{2,5}$
(2) Oxathia[4.3.3]-propellene.$HgCl_2$	0·554	62·1	89·1	$B_{2,5}$
(3) Dithia[4.3.3] propellene disulfoxide.H_2O	0·624	60·3	90·0	$B_{2,5}$
(4) Dithia[4.3.3]propellene disulfoxide	0·422	333·9	48·4	On the pathway from ${}^1H_6$ to ${}^1E$
(5) Cyclohexene	0·478	330·0	49·7	${}^1H_6$
(6) Bis(dithia[4.3.3]-propellene).$CdCl_2$	0·401 0·404	330·1 324·5	49·0 46·1	On the pathway from ${}^1H_6$ to E_6
(7) Dithia[4.3.3]propellene.-$HgCl_2$	0·305	319·3	50·0	
(8) Bis(oxathia[4.3.3]-propellene).$PdCl_2$	0·375	310·4	47·9	

* Boeyens' (1978) terminology is as follows: *C* chair, *B* boat, *H* half-chair, *E* envelope, *S* screw-boat. The sub- and superscripts give the numbers of the atoms below and above planar portions of the molecules.

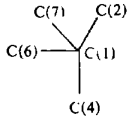
Table 6. *Values of Θ and Φ for the various dithia*[*n*.3.3]*propellane*(*ene*) *moieties with thiolane rings of symmetry m* (*fuller details have been deposited*)

Θ is the dihedral angle between the planes of the four carbon atoms in the two thiolane rings of the moiety. Φ is the dihedral angle between the envelope and its flap [*i.e.* between the planes C(1)–C(2)–C(3)–C(4) and C(2)–S–C(3)] for each of the thiolane rings.

n	Compound	Θ (°)	Φ (°)
1	Dithia[3.3.1]propellane	138·5, 137·7	156·2; 159·3; 157·5; 156·5
	Dithia[3.3.1]propellane.$HgCl_2$	141·1	164·8
	Dithia[3.3.1]propellane.$2I_2$	138·2	166·3; 151·3
	Dithia[3.3.1]propellane disulfoxide	136·5	143·7; 152·0
	Mean for $n = 1$	138·4 (1·7)	156·2 (7·4)
2	Dithia[3.3.2]propellane.$2I_2$	125·5	139·4; 147·5
	{(Dithia[3.3.2]propellane)$_2$Pd}Cl_2.$4H_2O$	122·9	138·4; 139·5
	Mean for $n = 2$	124·2 (1·8)	141·2 (4·2)
3	Dithia[3.3.3]propellane	120·0	138·2; 137·7
	Dithia[3.3.3]propellane.$HgCl_2$	121·3	132·9; 134·9
	Dithia[3.3.3]propellane.$PdCl_2$	119·1	138·4; 139·8
	{(Dithia[3.3.3]propellane)$_2$Pd}Cl_2.$4H_2O$	120·0	140·6; 139·9
	Mean for $n = 3$	120·1 (0·9)	137·8 (2·7)
4	Dithia[4.3.3]propellene.$PdCl_2$	118·9	138·7; 140·8
	Oxathia[4.3.3]propellene.$HgCl_2$	117·0	131·9(S); 136·3(O)
	Dithia[4.3.3]propellene disulfoxide (in the monohydrate)	119·0	140·6; 141·4
	Mean for $n = 4$	118·3 (1·1)	138·2 (3·6)

Table 7. *Averaged values of the bond angles* (°) *at the conjoining carbon atoms of the dithia*[3.3.*n*]*propellanes whose structures are reported in this paper*

Fuller details have been deposited. The atom numbering is that used in the diagrams. Angles C(2)–C(1)–C(7), C(6)–C(1)–C(7) and C(2)–C(1)–C(4), C(4)–C(1)–C(6) have been averaged pairwise.



	$n = 1$	$n = 2$	$n = 3$	$n = 4$ staggered	$n = 4$ eclipsed
C(2)–C(1)–C(6)	119·5 (8) [5]	113·4 (-) [2]	110·9 (4) [4]	111 (1) [7]	110·2 (1) [3]
C(2)–C(1)–C(7)	118·2 (8) [10]	116 (1) [4]	113 (1) [8]	111 (2) [12]	111 (2) [6]
C(2)–C(1)–C(4)	113 (1) [10]	109·5 (7) [4]	107·9 (3) [8]	106 (1) [14]	106 (3) [6]
C(4)–C(1)–C(7)	59·7 (4) [5]	89·1 (-) [2]	104·3 (5) [4]	113 (1) [5]	113 (1) [3]

trapezoidal with the conjoining (propeller) bond long at 1·572 (1) Å and the bond opposite to it short at 1·531 (2) Å; the length of the bond joining them is 1·554 (15) Å, close to that found in cyclobutane itself [1·548 (3) Å]. Allen (1984*a*, *b*) has found that exocyclic non-H substituents increase the C(1)–C(2) bond length by ~0·01 Å for each *cis*-1,2 interaction and by ~0·004 Å for each *trans*-1,2 interaction. For a [3.3.2]propellane this amounts to an increase of 0·028 Å, in excellent agreement with our experimental results.

The C_5 rings (four examples) all have exact or approximate *m* symmetry. There are no significant differences in C–C bond lengths; the angle in the flap of the envelope, ∠C(7)–C(8)–C(9), is ~3° less than the other bond angles. The torsion angles are close to the ideal values, with a smaller range than was found for thiolane rings.

Among the C_6 (cyclohexene) rings we find three propellenes where the rings have *m* symmetry and six with 2 symmetry (there is disorder in two of the 2 examples). The C=C double bond maintains its characteristic bond length (~1·33 Å) in the ordered crystals* and its torsion angle is close to 0°. The C(7)–C(8) bond length is ~0·06 Å shorter than the other C–C single bonds in the cyclohexene ring, as one would expect for sp^3–sp^2 bonds compared to

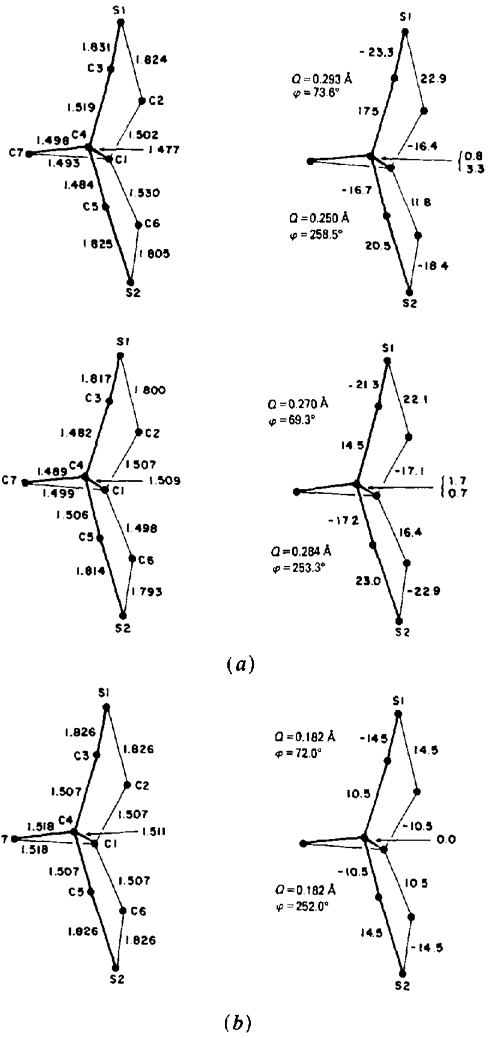


Fig. 26. Bond lengths (Å), torsion angles (°) and puckering parameters in dithia[3.3.1]propellane moieties; note that here and in the following figures there are in general three torsion angles about the conjoining bond [C(1)–C(4)]. The sequence (top to bottom) of values given in the diagram is thiolane-S(1) ring, thiolane-S(2) ring, aliphatic ring; fewer values indicate that some are equal because of symmetry. E.s.d.'s of torsion angles were calculated according to Stanford & Waser (1972). *Q* (Å) and *φ* (°) values for five-membered rings and *Q* (Å), *θ* (°), *φ* (°) values for six-membered rings, as calculated by the program *RING* (Cremer, 1979), are appended to the appropriate rings. (*a*) Dithia[3.3.1]propellane. σ(C–S), σ(C–C) ~0·01 Å, σ(∠C–S–C) ~ 0·4°, σ(∠C–C–C) ~ 0·7°, σ[τ(C–C–C–C)] ~ 0·7°. (*b*) Dithia[3.3.1]propellane.$HgCl_2$ (the propellane moiety has *mm*2 symmetry). σ(C–S) ~ 0·011 Å, σ(C–C) ~ 0·013 Å, σ(∠C–S–C) ~ 0·3°, σ(∠C–C–C) ~ 0·6°, σ[τ(C–C–C–C)] ~ 0·7°.

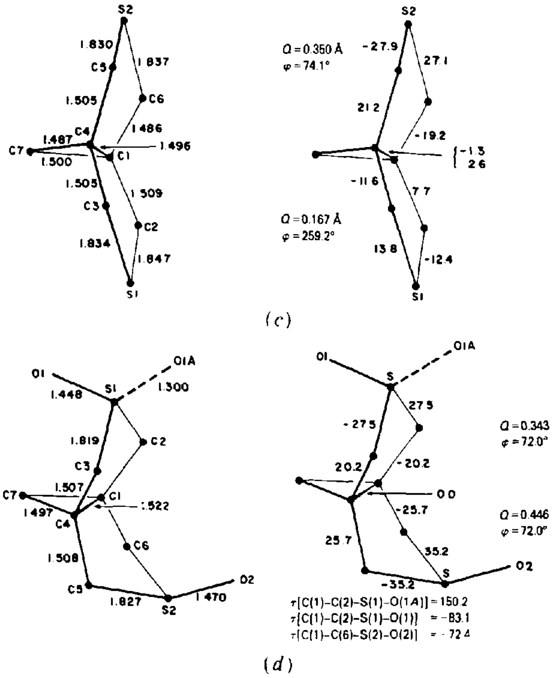


Fig. 26 (*cont.*) (*c*) Dithia[3.3.1]propellane.$2I_2$. σ(C–S) ~ 0·009 Å, σ(C–C) ~ 0·011 Å, σ(∠C–S–C) ~ 0·4°, σ(∠C–C–C) ~ 0·7°, σ[τ(C–C–C–C)] ~ 0·9°. (*d*) Dithia[3.3.1]propellane disulfoxide, major and minor stereoisomers. The moieties have mirror planes passing through O(1), S(1), C(7), S(2) and O(2). The bond lengths in the minor stereoisomer [position of O(1)*A* shown by broken line] were set equal to the values determined for the major stereoisomer and only the position of O(2) was allowed to differ in the refinement [§ III(xvii)]. σ(S–O) ~ 0·005 Å, σ(C–C) ~ 0·008 Å, σ(∠C–S–O) ~ 0·2°, σ(∠C–C–C) ~ 0·2°, σ[τ(C–C–C–C)] ~ 0·4°.

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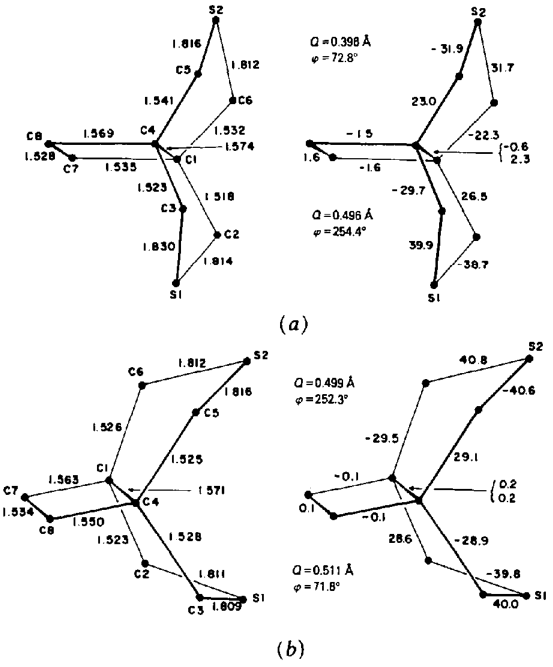
* There are indications of systematic errors affecting the peripheral atoms of the C_6 rings in dithia[4.3.3]propellene disulfoxide (Fig. 29*c*), bis(oxathia[4.3.3]propellene).$PdCl_2$ (Fig. 31*c*) and bis(dithia[4.3.3]propellene).$CdCl_2$ (especially molecule *A*; Fig. 31*d*). Correction has not been attempted.

sp^3–sp^3 bonds. There is a clear bond-angle difference between the two conformations: C(7)–C(8)–C(9) is ~119° for the *m* conformation but ~124° for the 2 conformation.

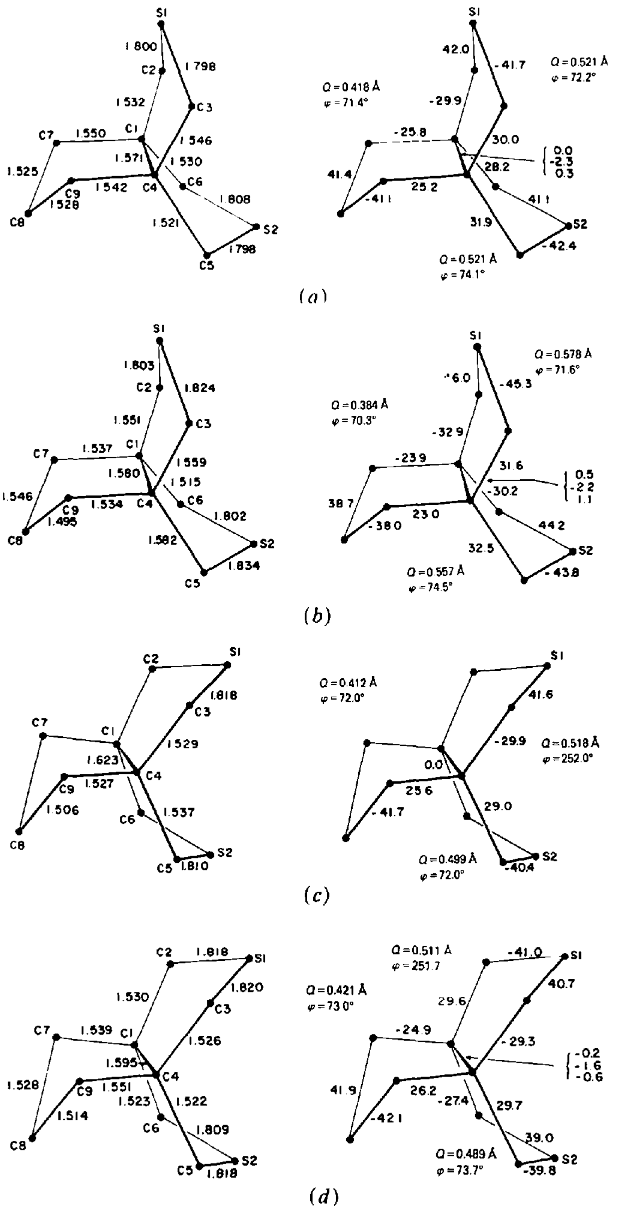
Our dimensions for the cyclohexene rings are generally rather similar to those reported for [4.4.2]propella-3,8-diene-11,12-dione (Fink, Van der Helm & Neely, 1975), for [4.4.4]propellatriene (Ermer, Gerdil & Dunitz, 1971) and for cyclohexene in the gas phase (Chiang & Bauer, 1969) (Fig. 31). However, the torsion angles show that the cyclohexene rings in dithia(and oxathia)[4.3.3]propellenes are somewhat flatter (less twisted) than those listed above, presumably owing to the restriction imposed by the conjoined thiolane rings.

In the dithia[3.3.1]propellanes, the central bond of the ring system is contracted by about 0·04 Å with respect to the standard C–C single-bond length of 1·542 Å; this is presumably due to the constraint imposed by the three-membered ring. In all the other dithia[*n*.3.3]propellanes(enes) ($n = 2, 3, 4$) with *m* (envelope) thiolane rings, the central bond is 0·03–0·06 Å *longer* than the standard value; analogous lengthening is found in [4.4.2]propella-3,8-diene-11,12-dione (Fink *et al.*, 1975). No such lengthening is found in the dithia[4.3.3]propellenes with thiolane rings of symmetry 2, where there is a staggered conformation about the central C–C bond. We ascribe the lengthening to the eclipsed conformations of all these molecules, as noted above explicitly for C_4 rings.


(*a*)

(*b*)

Fig. 27. Bond lengths (Å), torsion angles (°) and puckering parameters in [3.3.2]propellane moieties. (*a*) Dithia[3.3.2]propellane.2I$_2$. σ(C–S) ~ 0·010 Å, σ(C–C) ~ 0·013 Å, σ(∠C–S–C) ~ 0·4°, σ(∠C–C–C) ~ 0·7°, $\sigma[\tau$(C–C–C–C)] ~ 0·7°. (*b*) Propellane moiety of the cation in [bis(dithia[3.3.2]propellane)palladium(II)]Cl$_2$.4H$_2$O. σ(C–S) ~ 0·003 Å, σ(C–C) ~ 0·004 Å, σ(∠C–S–C) ~ 0·2°, σ(∠C–C–C) ~ 0·3°, $\sigma[\tau$(C–C–C–C)] ~ 0·3°.


(*a*)

(*b*)

(*c*)

(*d*)

Fig. 28. Bond lengths (Å), torsion angles (°) and puckering parameters in dithia[3.3.3]propellane moieties. (*a*) Dithia[3.3.3]propellane. σ(C–S) ~ 0·003 Å, σ(C–C) ~ 0·004 Å, σ(∠C–S–C) ~ 0·1°, σ(∠C–C–C) ~ 0·2°, $\sigma[\tau$(C–C–C–C)] ~ 0·3°. (*b*) Dithia[3.3.3]propellane.HgCl$_2$. σ(C–S) ~ 0·017 Å, σ(C–C) ~ 0·021 Å, σ(∠C–S–C) ~ 0·9°, σ(∠C–C–C) ~ 1·2°, $\sigma[\tau$(C–C–C–C)] ~ 1·4°. (*c*) Dithia[3.3.3]propellane.PdCl$_2$ - molecule has a mirror passing through S(1), S(2), C(8). σ(C–S) ~ 0·006 Å, σ(C–C) ~ 0·008 Å, σ(∠C–S–C) ~ 0·4°, σ(∠C–C–C) ~ 0·5°, $\sigma[\tau$(C–C–C–C)] ~ 0·7°. (*d*) Propellane moiety of the cation in [bis(dithia[3.3.3]propellane)palladium(II)]Cl$_2$.4H$_2$O. σ(C–S) ~ 0·003 Å, σ(C–C) ~ 0·005 Å, σ(∠C–S–C) ~ 0·1°, σ(∠C–C–C) ~ 0·3°, $\sigma[\tau$(C–C–C–C)] ~ 0·3°.

(iv) *The actual conformations of the rings.* The approximation that thiolane and aliphatic C_5 rings have envelope (m) or twist (2) conformations has been used as a convenient basis for much of the prior discussion in this paper. However, there are significant deviations from ideal symmetries in most of the molecules studied and these are now considered in terms of the ring puckering coordinates introduced by Cremer & Pople (1975), whose treatment we follow.* The four-membered rings in the molecules encountered here are all essentially planar so explicit discussion is not needed. The five-membered rings are described by a single amplitude-phase pair (Q, φ) and the displacement expression is:

$$z_j = (\tfrac{2}{5})^{1/2} Q \cos[\varphi + 4\pi(j-1)/5].$$

The values of $\varphi = 0$, 36, 72°... correspond to ten envelope conformations with m symmetry, while the values of $\varphi = 18$, 54, 90°... correspond to ten twist conformations with 2 symmetry [*cf.* Figs. 9·8 and 9·9 of Dunitz (1979)]. In cyclopentane itself the potential energy is essentially independent of φ and the forms interconvert by pseudorotation; in thiolane appreciable potential barriers separate the conformers and pseudorotation does not occur.

For six-membered rings there are three puckering degrees of freedom, which are described by a single amplitude-phase pair (q_2, φ) and a single puckering coordinate (q_3). The displacement expression is:

$$z_j = (\tfrac{2}{6})^{1/2} q_2 \cos[\varphi + 4\pi(j-1)/6] + [(-1)^{j-1}/\sqrt{6}]q_3.$$

The parameters q_2, q_3 and φ are conveniently replaced by a 'spherical polar set' (Q, θ, φ) where Q is the total puckering amplitude and θ is an angle

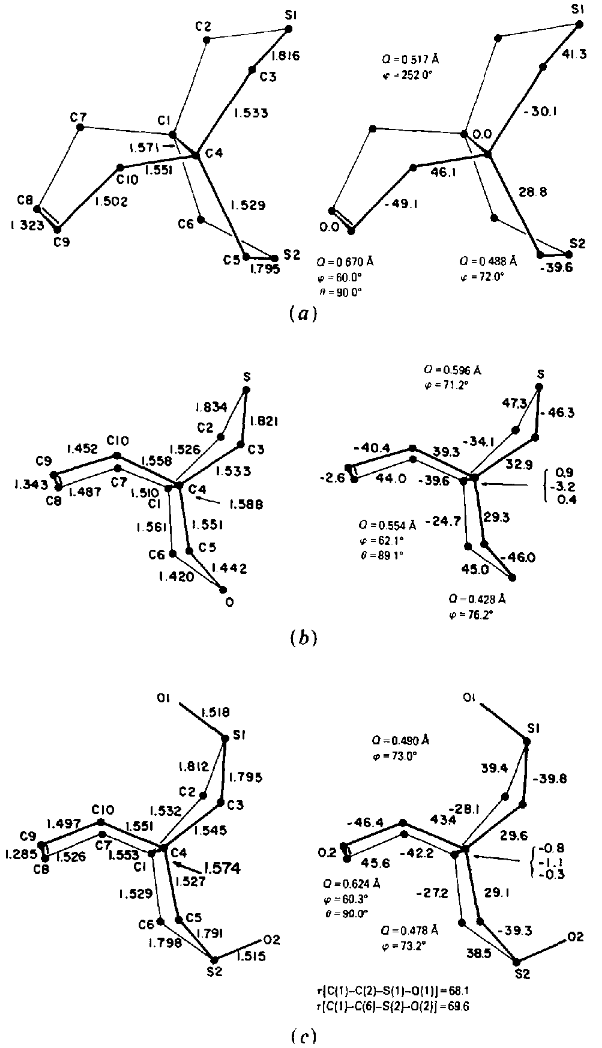


Fig. 29. Bond lengths (Å), torsion angles (°) and puckering parameters in eclipsed [4.3.3]propellene moieties. (*a*) Dithia[4.3.3]propellene.$PdCl_2$. The propellene moiety is bisected by a mirror plane through the two S atoms. $\sigma(C–S) \sim 0·006$ Å, $\sigma(C–C) \sim 0·009$ Å, $\sigma(\angle C–S–C) \sim 0·2°$, $\sigma(\angle C–C–C) \sim 0·4°$, $\sigma[\tau(C–C–C–C)] \sim 0·6°$. (*b*) Oxathia[4.3.3]propellene, as found in its $HgCl_2$ complex. $\sigma(C–S) \sim 0·010$ Å, $\sigma(C–C) \sim 0·014$ Å, $\sigma(\angle C–S–C) \sim 0·4°$, $\sigma(\angle C–C–C) \sim 0·8°$, $\sigma[\tau(C–C–C–C)] \sim 1·1°$. (*c*) Dithia[4.3.3]propellene disulfoxide, as found in the crystalline monohydrate. $\sigma(C–S) \sim 0·005$ Å, $\sigma(C–C) \sim 0·007$ Å, $\sigma(\angle C–S–C) \sim 0·2°$, $\sigma(\angle C–C–C) \sim 0·4°$, $\sigma[\tau(C–C–C–C)] \sim 0·5°$.

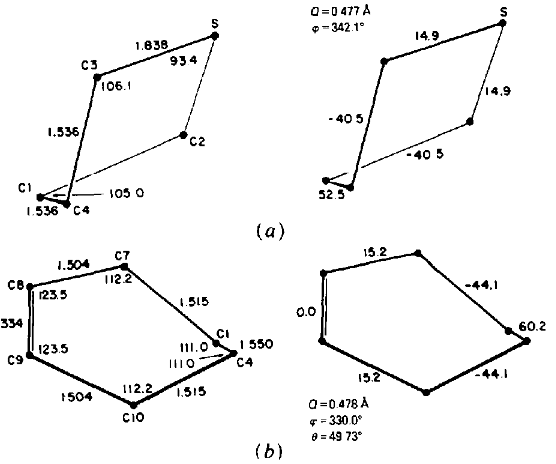


Fig. 30. Dimensions (Å, °) and ring puckering parameters calculated for (*a*) thiolane [from data of Nahlovska, Nahlovsky & Seip (1969)] and (*b*) cyclohexene [from data of Chiang & Bauer (1969)]. The schematic diagrams match those in the following figures.

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* Dunitz (1979) gives an excellent introduction to the description of ring conformations. The relation between Altona-Sundaralingam and Cremer-Pople ring puckering parameters has been discussed by Rao, Westhof & Sundaralingam (1981), Essen & Cremer (1984) and Cremer (1984). Rao, Westhof & Sundaralingam (1981) and Taylor (1980) give expressions for the standard deviations of the ring puckering parameters. Ring asymmetry parameters have been used by Nardelli (1983).

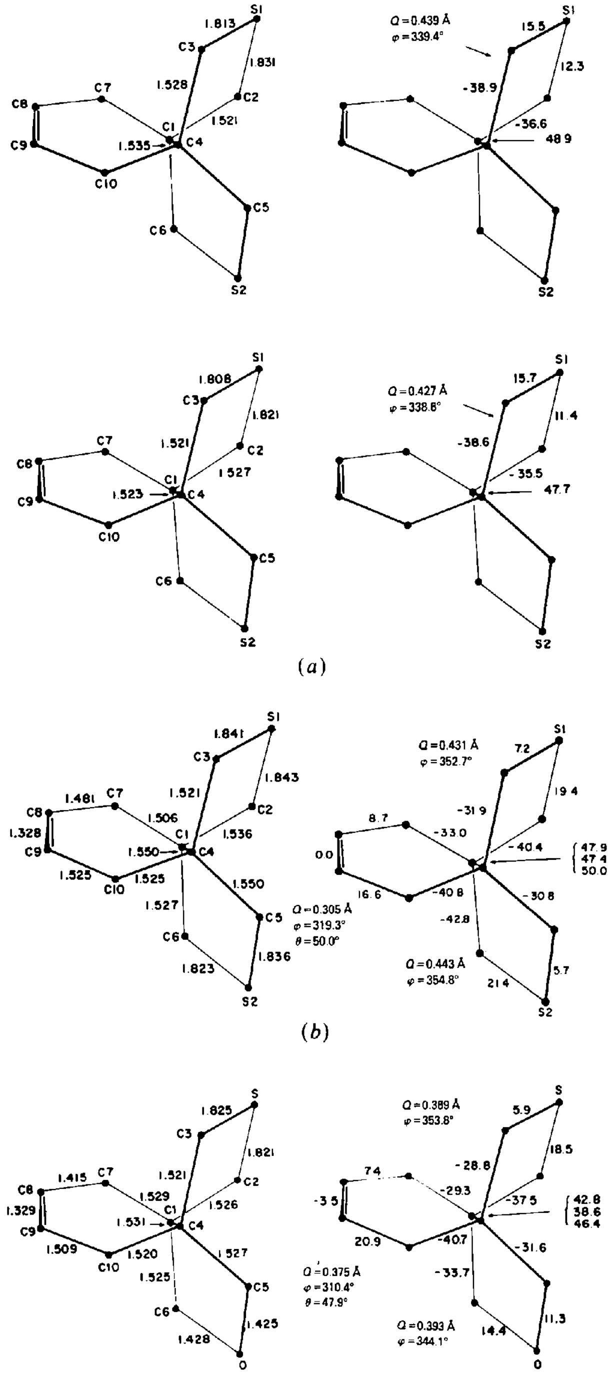

Fig. 31. Bond lengths (Å), torsion angles (°) and puckering parameters in staggered dithia[4.3.3]propellene moieties. (*a*) Dithia[4.3.3]propellene - both molecules in the asymmetric unit are disordered by interchange of thiolane-S(2) and cyclohexene rings. Thus dimensions and e.s.d.'s are given only for the thiolane-S(1) ring. $\sigma(\text{S–C}) \sim 0.005$ Å, $\sigma(\text{C–C}) \sim 0.006$ Å, $\sigma(\angle\text{C–S–C}) \sim 0.2°$, $\sigma(\angle\text{C–C–C}) \sim 0.4°$, $\sigma[\tau(\text{C–C–C–C})] \sim 0.4°$. (*b*) Dithia[4.3.3]propellene.$HgCl_2$. $\sigma(\text{S–C}) \sim 0.019$ Å, $\sigma(\text{C–C}) \sim 0.030$ Å, $\sigma(\angle\text{C–S–C}) \sim 0.9°$, $\sigma(\angle\text{C–C–C}) \sim 1.6°$, $\sigma[\tau(\text{C–C–C–C})] \sim 1.5°$. (*c*) Bis(oxathia[4.3.3]propellene).$PdCl_2$. $\sigma(\text{S–C}) \sim 0.008$ Å, $\sigma(\text{C–C}) \sim 0.01$ Å, $\sigma(\angle\text{C–S–C}) \sim 0.3°$, $\sigma(\angle\text{C–C–C} \sim 0.6°$, $\sigma[\tau(\text{C–C–C–C})] \sim 0.9°$.

$(0 \leq \theta \leq \pi)$ such that

$$q_2 = Q \sin \theta$$

$$q_3 = Q \cos \theta.$$

This coordinate system allows the mapping of all types of puckering (for a given amplitude Q) on the surface of a sphere. A complete set of diagrams and a consistent nomenclature have been proposed by Boeyens (1978), who gives references to earlier work.

It is essential to use a standard numbering system (see Fig. 1 and diagrams of the molecules) in a standard way in order to achieve consistent intercomparison of the geometrical features of the eighteen molecules studied here. The following sequences were

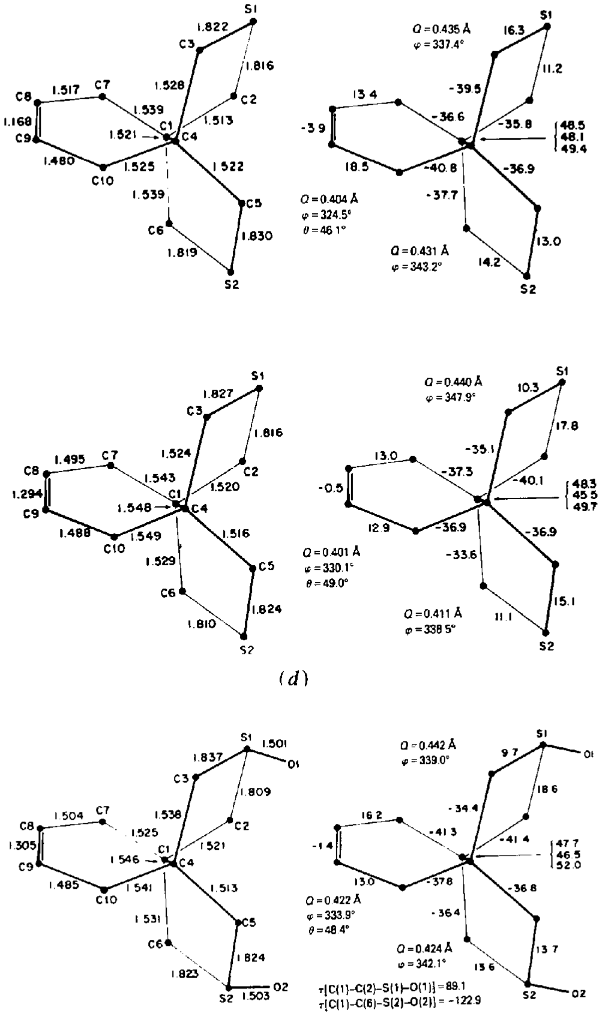

Fig. 31 (*cont.*) (*d*) Bis(dithia[4.3.3]propellene).$CdCl_2$ - two molecules in the asymmetric unit. $\sigma(\text{C–S}) \sim 0.007$ Å, $\sigma(\text{C–C}) \sim 0.01$ Å, $\sigma(\angle\text{C–S–C}) \sim 0.3°$, $\sigma(\angle\text{C–C–C}) \sim 0.5°$, $\sigma[\tau(\text{C–C–C–C})] \sim 0.8°$. (*e*) Dithia[4.3.3]propellene disulfoxide. $\sigma(\text{C–S}) \sim 0.004$ Å, $\sigma(\text{C–C}) \sim 0.006$ Å, $\sigma(\angle\text{C–S–C}) \sim 0.2°$, $\sigma(\angle\text{C–C–C}) \sim 0.4°$, $\sigma[\tau(\text{C–C–C–C})] \sim 0.7°$.

used here for the atoms of the rings:

S(1) ring: C(1), C(2), S(1), C(3), C(4).

S(2) ring: C(1), C(6), S(2), C(5), C(4).

Aliphatic ring: C(1), C(7), C(8), C(9), C(10),* C(4).

The amplitude and phase-angle values are entered on the various diagrams; the Q, φ values for all the five-membered rings are collected together in Fig. 33. The rings with envelope conformation all have $\varphi \sim 72$ or 252° [these particular values of 0(mod 36)° are, of course, determined by the numbering convention used]; similarly the twist rings all have $\varphi \sim 342°$. The envelope rings have a broad distribution in puckering amplitude and a narrow distribution in phase angle. This shows that the envelope rings can invert their conformations by passing through a planar conformation ($Q = 0$ Å). This ring flattening inversion pathway has already been noted by Murray-Rust & Motherwell (1978) in their study of the β-1′-aminofuranoside fragment of nucleosides and nucleotides. There is no indication in our results of a pseudorotational pathway for rings in the envelope conformation. However, the converse situation applies to the rings in twist conformation, where the pseudorotational interconversion pathway is indicated but not that of ring flattening.

Q values of ~0·5 Å, above the average for envelope rings, are found in some of the Pd complexes and can be ascribed to the S···Pd···S interactions; however, the largest value of Q (0·596 Å) is found in oxathia[4.3.3]propellene.HgCl$_2$ and the reason for this is not clear.

The smallest Q values are found for the rings in the [3.3.1] molecules, as has already been noted in Table 6. A striking example of an almost flat cyclopentane ring is found in 8,8-dichlorotricyclo[3.2.1.0^{1,5}]octane ($C_8H_{10}Cl_2$) (Wiberg, Burgmaier, Shen, La Placa, Hamilton & Newton, 1972) where $Q = 0{\cdot}093$ Å, $\varphi = 72°$ [alternatively Φ, the flap angle of the envelope, is 170 (3)°]. Wiberg *et al.* (1972) have suggested that this flattening is a consequence of the distortion from ideal tetrahedral arrangements at the bridgehead atoms of the conjoining bond, which is also found in the present molecules, particularly for $n = 1, 2$ (Table 7). Thus the flattening of thiolane rings in dithia[3.3.1]propellanes studied here can also be ascribed to the deformations of the bond angles at the conjoining carbons. One should note that the considerable spread in the flap angle (Φ) values given in Table 6 is presumably to be ascribed to crystal packing effects.

The puckering parameters for the cyclohexene rings are given in Table 5. The rings with m symmetry have the $B_{2,5}$ (boat) conformation of Boeyens' (1978) Fig. 1; there are no indications of a transformation pathway. The rings with 2 symmetry in cyclohexene and bis(dithia[4.3.3]propellene).CdCl$_2$ have Boeyens' $^3H_6$ (half-chair) conformation; the rings in dithia[4.3.3]propellene.HgCl$_2$ and, especially, bis(oxathia[4.3.3]propellene).PdCl$_2$ approach the E_6 (envelope) conformation, while that in (neat) dithia[4.3.3]propellene disulfoxide is slightly on the reverse pathway to the ^1E conformation.

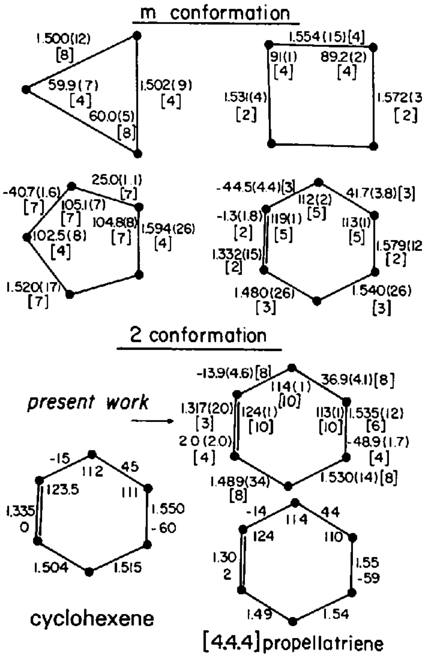

Fig. 32. Average values for the dimensions of the aliphatic rings of the propellane(ene) moieties (sulfoxides excluded).

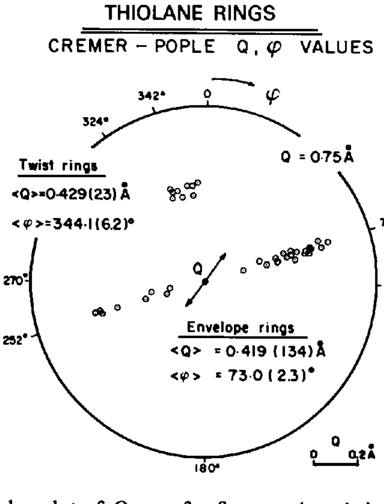

Fig. 33. Polar plot of Q *vs* φ for five-membered rings. The outer circle corresponds to $Q = 0{\cdot}75$ Å. The points along the diameter from 72 to 252° are for rings with envelope conformations; the other group of points is for twist rings.

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* If present.

(2) *The dithia(and oxathia)[n.3.3]propellane(ene) moieties*

We first summarize and compare the various geometries found for each dithia(and oxathia)-[*n*.3.3]propellane(ene) ($n = 1-4$). We then consider the conformations found for each of the propellane molecules, compare them with what is theoretically possible, and discuss differentiation among the various molecules on the basis of the patterns of torsion angles that are found.

(i) *Dithia*[3.3.1]*propellane, its complexes and its disulfoxide.* There are five examples (two crystallographically independent molecules in the neat crystals, the $2I_2$ complex, the $HgCl_2$ complex and the disulfoxide) and the propellane moiety has the same conformation in the first four (see Fig. 34). In the bis(diiodine) complexes only one lone pair at each sulfur interacts with iodine; at one S (shown as the upper S in Fig. 34) the axial lone pair interacts with iodine whereas at the lower S it is the equatorial lone pair. The dithia[3.3.1]propellane.$2I_2$ moiety has symmetry *m*. In the $HgCl_2$ complex the axial and equatorial lone pairs of both sulfurs interact, each with a different mercury atom. Thus four different mercury atoms interact with a particular dithia[3.3.1]propellane moiety. The conformations of the sulfoxides are different as the flaps of the two envelopes of the thiolane oxide rings are oppositely disposed with reference to the C_3 ring. The major and minor dithia[3.3.1]propellane disulfoxide stereoisomers differ in that the oxygens are both linked *via* equatorial lone pairs in the minor isomer, but *via* an axial and an equatorial lone pair in the major isomer.

(ii) *Dithia*[3.3.2]*propellane complexes.* The neat crystals are plastic and of very poor diffraction quality. The bis(diiodine) complex has the same overall structure as dithia[3.3.1]propellane.$2I_2$ [§ IV(2)(i) and Fig. 34] and an analogous overall conformation is found in [4.4.2]propella-3,8-diene-11,12-dione (Fink, van der Helm & Neely, 1975) where the cyclohexenes are boats and the cyclobutanedione is planar. The cations in the salts {bis(dithia[*n*.3.3]propellane)palladium(II)}$Cl_2.4H_2O$ ($n = 2, 3$) have the same structure which is shown in Fig. 35 [§ IV(2)(iii)]. The axial lone pairs of the sulfurs interact with Pd in these cations.

(iii) *Dithia*[3.3.3]*propellane and its complexes.* Structures are shown in Fig. 35 for the four examples known. In the free molecules and the $HgCl_2$ complex the propellane moiety has quasi-C_3 (3) symmetry (*i.e.* ignoring the difference between S and CH_2). The arrangement in the $PdCl_2$ molecular complex and the Pd^{2+} cation is the same as that noted above for {bis-(dithia[3.3.2]propellane)palladium(II)}$Cl_2.4H_2O$.

(iv) *Dithia(and oxathia)*[4.3.3]*propellene and its complexes.* There are four examples with *m* symmetry. The arrangement in dithia[4.3.3]propellene.$PdCl_2$ is the same as that in the other $PdCl_2$ molecular complexes and Pd^{2+} cations (Fig. 35). In the $HgCl_2$ complex of oxathia[4.3.3]propellene the propellene moiety has quasi-C_{3h} ($3/m$) symmetry if we take into account only the directions of folding of the envelope flaps; Hg interacts with equatorial lone pairs of S. Thus the conformation of the complex is analogous to that found for dithia[3.3.3]propellane.$HgCl_2$ (see Fig. 35). Dithia[4.3.3]propellene disulfoxide (as it appears in the monohydrate) has quasi-C_{3h} ($3/m$) symmetry (Fig. 29*c*); the oxygens are both linked *via* axial lone pairs of the sulfurs, and the molecular configuration thus differs from those found in dithia[3.3.1]propellane disulfoxide (Figs. 34 and 26*d*).

The two thiolane rings are in the 2 conformation and the cyclohexene rings are approximate half-chairs (see Table 5) in the other six examples {neat dithia[4.3.3]propellene (not quantified because of disorder), its $HgCl_2$ and $CdCl_2$ complexes (two independent molecules), the {oxathia[4.3.3]propellene}$_2$.$PdCl_2$ complex and neat dithia[4.3.3]propellene disulfoxide (Fig. 36)}.

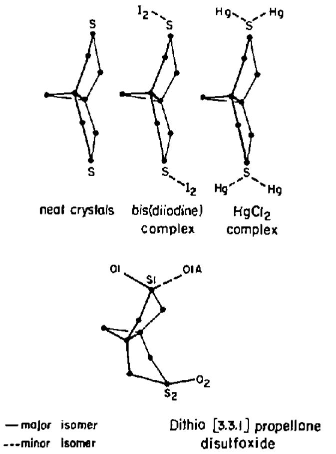

Fig. 34. Conformations of the dithia[3.3.1]propellane moiety.

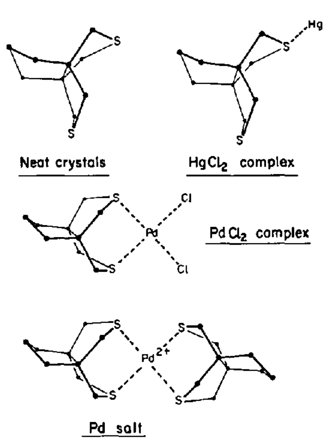

Fig. 35. Conformations of the dithia[3.3.3]propellanes.

(3) *The molecular* (*ionic*) *moieties*

(i) *Molecular-mechanics calculations.* Qualitative considerations, made with the aid of flexible molecule models,[*] lead to explanations of many features of the overall geometries of the dithia[n.3.3]propellane(ene) moieties. When the thiolane rings have the m conformation, there is an eclipsed arrangement about the central C–C bond, while there is a concerted twist towards the staggered arrangement for the 2 conformation. A combination of m and 2 thiolane-ring conformations could not be sustained about the central bond without considerable bond-angle distortion and does not occur. Furthermore, a 2 conformation for the thiolane rings in dithia[n.3.3]propellanes ($n = 1$, 2, 3) would require a staggered arrangement about the central C–C bond; this is clearly not possible when $n = 1$ and unlikely when $n = 2$. Qualitative considerations do not explain the absence of the 2 conformation for $n = 3$, nor the appearance of both conformations when $n = 4$. We have thus supplemented the qualitative study by quantitative molecular-mechanics calculations [Burkert & Allinger, 1982; program *MM*2 (QCPE No. 395)].

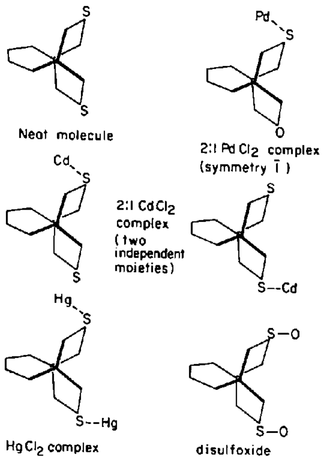

Fig. 36. Conformations of dithia(and oxathia)[4.3.3]propellenes, with rings in 2 conformation.

No *MM*2 calculations could be made for $n = 1$ conformers because of a lack of appropriate parameters for the three-membered ring; this is unfortunate because the most definite evidence for influence of the aliphatic rings on geometrical parameters of the thiolane rings appears when $n = 1$. The disulfoxides were also omitted because of a lack of parameters. The various contributions to the steric energy for the conceivable conformers for $n = 2$, 3, 4 are detailed in a deposited table. The largest contributions come from bending and torsional strains; the differences among the conformers are small and contributions from a particular type of strain are nowhere decisive. The overall steric energies are summarized in Fig. 37. In all the moieties the conformer found experimentally is that with the lowest calculated steric energy. Complexation with palladium is essential for the stabilization of the *anti,anti* conformer (No. 4 in Fig. 37);[*] 13–20 kJ mol^{-1} are needed to stabilize this conformer. The calculations show that the 2 conformer of dithia[3.3.3]propellane is ~20 kJ mol^{-1} less stable than the *anti,syn* (m) conformer, and this is in agreement with the non-appearance of the 2 conformer among the experimental results. Conversely the 2 conformer is the most stable when $n = 4$, both

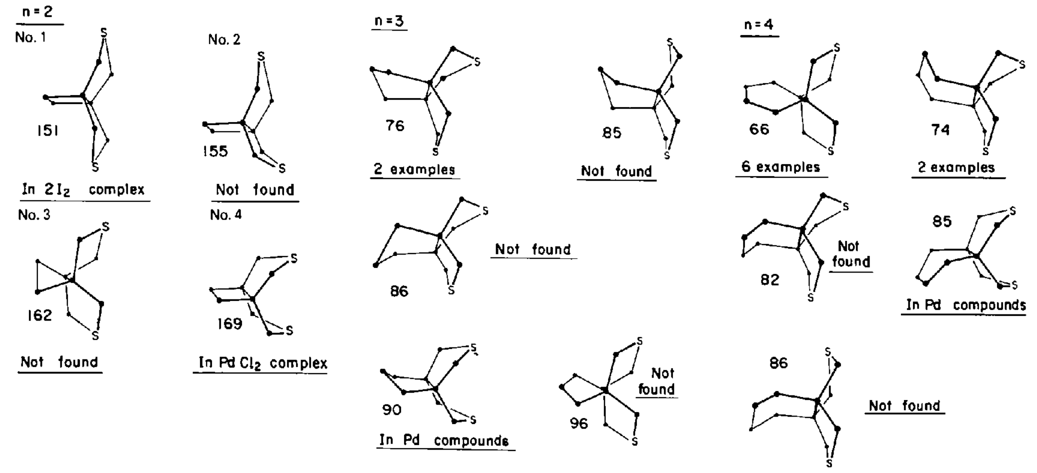

Fig. 37. Steric energies (kJ mol^{-1}) for various conformers of dithia[n.3.3]propellanes(enes). The steric energies are defined by Burkert & Allinger (1982) and calculated by program *MM*2. Energies are intercomparable for particular values of n, not between different values of n.

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[*] We have found HGS molecular models (Benjamin-Maruzen) convenient.

[*] An analogous overall molecular structure is found in 1-cyanotetracyclo[3.3.1.1^{3,7}.0^{3,7}]decane (Gibbons & Trotter, 1973) which can be considered as a [3.3.1]propellane derivative with an *anti,anti* arrangement stabilized by a CH_2 group instead of a $PdCl_2$ group.

examples with the *anti,syn* (*m*) conformation – oxathia[4.3.3]propellene.$HgCl_2$ and dithia[4.3.3]propellene disulfoxide monohydrate – being possibly stabilized by interaction with Hg or H_2O, respectively. Calculated values of bond lengths, angles and torsion angles agree reasonably well with the averaged experimental values [see also § IV(3)(ii)].

*MM*2 calculations have been reported recently for [*l.m.n*]propellanes with *l*, *m*, *n* equal to 2, 3, 4 (Dodziuk, 1984); calculations for [3.3.2]-, [3.3.3]- and, to a lesser extent, [4.3.3]propellanes should be directly comparable with our present crystallographic and calculated (*MM*2) results. Unfortunately the overall conformations used in the Dodziuk calculations were not specified except for [3.3.2]propellane where it was noted that *syn,syn* (corresponding to her formula XV*b*) and *syn,anti* (XV*a*) conformers were stable while the *anti,anti* (XV*c*) conformer was not. These conclusions agree partly with our results summarized in Fig. 37; the *syn,syn*, conformer (No. 1) is found while the *syn,anti* (No. 2) is not, the *anti,anti* (No. 4) conformer appearing only when stabilized by S···Pd interactions.

(ii) *Influence of the size of the aliphatic ring on the geometry of the molecule as a whole* (*the 'Klammer' effect*). Consider only the dithia[*n*.3.3]propellane(ene) moieties where the thiolane rings have *m* symmetry; let Θ be the angle between the best planes of the four carbons in each of the thiolane rings of such moieties.* Ideally $\Theta = 120°$ but it is predicted that Θ will exceed the ideal value as *n* becomes smaller; this is the 'Klammer' effect. Values of Θ are summarized in Table 6; for $n = 1$, $\Theta \sim 140°$, for $n = 2$, $\Theta \sim 124°$ and for $n = 3$, 4, $\Theta \sim 120°$. We can make other tests of the 'Klammer' effect by using published results for various substituted propellenes(anes) containing aliphatic and other rings of different sizes (Table 8). The values of Θ follow the same general pattern as shown in Table 6; we have not attempted to explain some of the obvious anomalies.

The second effect of small ring size has already been referred to above: the marked flattening of the thiolane rings (and their increased flexibility) found when $n = 1$; more evidence is needed to show whether a similar but much smaller effect occurs when $n = 2$.

We have used the atomic coordinates obtained in the molecular-mechanics steric energy minimization calculations of § IV(3)(i) to calculate values of Θ for those conformers found experimentally. For $n = 2$ we obtain $\Theta \sim 127°$ and for $n = 3$, $\Theta \sim 119°$ (there is a range of ~0·5° for different conformers with the same value of *n*). Thus there is good agreement between observed and calculated values of Θ.

Table 8. *Values for Θ for some other propellanes with an eclipsed conformation*

Θ is defined as the angle between the two planes which have the conjoining (propeller) bond in common.

n	Compound	Θ (°)	Reference
1	Tetracyclo[6.2.2.1^{2,7}.0^{2,7}]trideca-3,5,9-triene-11,12-dione	138	(*a*)
	([4.4.1]Propella-2,4-diene)-(*N*-methyl-1.2,4-triazoline-3,5-dione) adduct	137·3	(*b*)
	14-Methyl-6-oxa-12,14,16-triazaheptacyclo[9.5.2.2^{3,9}.1^{2,10}.0^{4,8}0^{12,16}]henicosa-17,19-diene-5,7,13,15-tetrone	136·1	(*c*)
	([4.3.1]Propella-2,4-diene)-(*N*-methyl-1,2,4-triazoline-3,5-dione) adduct	134·1	(*c*)
	([4.2.1]Propella-2,4-diene)–(*N*-methyl-1,2,4-triazoline-3,5-dione) adduct	128·2	(*c*)
2	[4.4.2]Propella-3,8-diene-11,12-dione	133	(*d*)
3	11,13-Dioxo-12-methyl-12-aza[4.4.3]propella-3,8-diene	126·2	(*e*)
	syn-8,9-Epoxy-11,13-dioxo-12-methyl-12-aza[4.4.3]propella-3-ene	125·7	(*f*)
	18-Ethoxy-15-methyl-5-phenyl-3,5,7,15-tetraazapentacyclo[7.4.3.2^{2,8}.0.0^{3,7}]-octadeca-17-ene-4,6,14,16-tetrone	123·8	(*g*)
	15-Methyl-5-phenyl-5,15-diazapentacyclo[7.4.3.2^{2,8}.0.0^{3,7}]octadeca-10,12,17-triene-4,6,14,16-tetrone	124·4	(*g*)
	12-Oxapentacyclo[8.4.3.2^{2,9}.0.0^{3,8}]-heptadeca-5,14,16,18-tetraene-4,7,11,13-tetrone	126·0	(*g*)
	5-Methyl-14,16-dioxa-3,5,7-triazapentacyclo[7.4.3.2^{2,8}.0.0^{3,7})octadeca-10,12,17-triene-4,6-dione	127·4	(*g*)
	5-Methyl-15-oxa-5-azapentacyclo[7.4.3.2^{2,8}.0.0^{3,7}]octadeca-10,12,17-triene-4,6-dione	123·6	(*g*)
	5,15-Dioxapentacyclo[7.4.3.2^{2,8}.0.0^{3,7}]octadeca-10,12,17-triene-4,6-dione	122·5	(*g*)
	5-Phenyl-3,5,7-triazapentacyclo[7.4.3.2^{2,8}.0.0^{3,7}]octadec-17-ene-4,6-dione	120·6	(*h*)
	5-Phenyl-15-thia-3,5,7-triazapentacyclo[7.4.3.2^{2,8}.0.0^{3,7}]octadec-17-ene-4,6,15-trione	117·6	(*i*)

References: (*a*) Kapon (1986); (*b*) Kaftory (1980*c*); (*c*) Kaftory (1978*c*); (*d*) Fink *et al.* (1975); (*e*) Kaftory & Dunitz (1976); (*f*) Kaftory, Dunitz & Mills (1976); (*g*) Kaftory (1980*a*); (*h*) Kaftory (1978*a*); (*i*) Kaftory (1978*b*).

(iii) *Summary of experimental results.* The propellane(ene) molecules (ions) studied here, and others, can be divided into two groups: those with an eclipsed conformation about the conjoining (propeller) bond, and those with a staggered conformation. This distinction appears to be categorical and we have encountered neither contradiction nor compromise on this point. There is a somewhat weaker corollary to this rule, which states that in the molecules considered in this section, the rings all have the same conformation. This corollary holds for all but three of the thirty-odd examples examined.

Among the dithia[*n*.3.3]propellanes(enes), and the corresponding oxathia and disulfoxide compounds, both thiolane rings always have *m* symmetry for $n = 1$, 2; for $n = 3$, all three rings have *m* symmetry. For $n = 4$ both symmetries are found for the thiolane rings and hence for the cyclohexene rings; however, all three rings have the same conformation in a particular molecule. The corollary that there is no mixing of ring conformations is strictly obeyed in the compounds investigated here, and also in other propellanes. Thus, in [4.4.2]propella-3,8-diene-11,12-dione (Fink, van der Helm & Neely, 1975), 11,13-dioxo-12-methyl-12-aza[4.4.3]propella-3,8-diene (Kaftory &

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* The reason for excluding the 2 conformation here is that such best planes, although calculable, will not have any physical significance.

Table 9. *Puckering parameters*

(*a*) Values of puckering parameters for the rings in three molecules which have been reported not to obey the non-mixing corollary (see text for discussion)

(*A*) Five-membered ring

Molecule	Q (Å)	φ (°)	Conformation	Reference
syn-2,3,4,5-Diepoxy-12-oxa[4.4.3]propellane (staggered about conjoining bond)	0·373	180·8	m	(*a*)

(B) Six-membered rings

Molecule	Q (Å)	φ (°)	θ (°)	Conformation following Boeyens (1978)*	Reference
syn-2,3,4,5-Diepoxy-12-oxa[4.4.3]propellane					
Diepoxy ring	0·362	149·5	112·6	$^{6}S_{1}$	
Cyclohexane ring	0·539	304·1	169·1	$^{4}C_{1}$ towards E_{3}	
([4.4.1]Propella-2,4-diene)–(*N*-methyl-1,2,4-triazoline-3,5-dione) adduct {(4.4.1)*P*} (eclipsed about conjoining bond)					(*b*)
Substituted ring	0·770	238·6	89·7	$^{2,5}B$	
Unsubstituted (cyclohexane) ring	0·502	336·1	131·6	$^{4}H_{3}$	
2-Hydroxy[4.2.2]propellane *p*-nitrobenzoate	0·537	333·6	139·5	$^{4}H_{3}$	(*c*)

(*b*) Values of puckering parameters for the rings in the *anti*-2,3,4,5-diepoxy-12-oxa[4.4.3]propellane molecule which has been incompletely described in the literature but which does obey the non-mixing corollary (see text for discussion); there are two crystallographically independent molecules (*A* and *B*) in the asymmetric unit and both molecules are staggered about the conjoining bond

(*A*) Five-membered rings

	Q (Å)	φ (°)	Conformation	Reference
Molecule *A*	0·386	348·4	close to 2	(*a*)
Molecule *B*	0·392	157·6	close to 2	

(*B*) Six-membered rings

	Q (Å)	φ (°)	θ (°)	Conformation following Boeyens (1978)
Diepoxy ring				
Molecule *A*	0·367	326·4	68·0	$^{1}S_{6}$
Molecule *B*	0·374	149·8	111·8	$^{6}S_{1}$
Cyclohexane ring				
Molecule *A*	0·523	184·6	14·7	$^{1}C_{4}$ towards E_{4}
Molecule *B*	0·523	2·6	166·9	$^{4}C_{1}$ towards ^{4}E

References: (*a*) Kaftory (1980*b*); (*b*) Kaftory (1980*c*); (*c*) Silverton *et al.* (1974)

* For Boeyens' (1978) notation see Table 5.

Dunitz, 1976) and *syn*-8,9-epoxy-11,13-dioxo-12-methyl-12-aza[4.4.3]propell-3-ene (Kaftory, Dunitz & Mills, 1976) the C_6 rings have nearly m symmetry and the overall conformation of the moiety is eclipsed and analogous to that shown in Figs. 26(*a–c*), and 27(*a*). The corollary is also followed in twelve other substituted propellanes with eclipsed arrangements about the conjoining central bond, as reported by Kaftory (1978*a*, *b*, *c*, 1980*a*, *c*). It is also followed in [4.4.4]propellatriene (Ermer, Gerdil & Dunitz, 1971) which has an overall staggered conformation with each of the three C_6 rings having nearly 2 symmetry. However, the non-mixing corollary breaks down, to a greater or lesser extent, in the eclipsed molecules ([4.4.1]propella-2,4-diene)-(4-methyl-1,2,4-triazoline-3,5-dione) adduct ([4.4.1]*P*) (Kaftory, 1980*c*), and 2-hydroxy[4.2.2]propellane *p*-nitrobenzoate (Silverton, Milne, Eaton, Nyi & Temme, 1974) and in the staggered molecule *syn*-2,3;4,5-diepoxy-12-oxa[4.4.3]propellane (Kaftory, 1980*b*). Although [4.4.1]*P* is eclipsed, the unsubstituted cyclohexane ring has a half-chair conformation, as is shown by the puckering parameters of Table 9 and in Fig. 6 of Kaftory (1980*c*). The 2-hydroxy[4.2.2]propellane *p*-nitrobenzoate molecule is nearly, but not exactly, eclipsed and the cyclohexane has a half-chair conformation (Table 9). The overall conformation taken up by a Benjamin–Maruzen model (see footnote on p. 592) is remarkably close to that of the actual molecule [see Fig. 2 of Silverton *et al.* (1974)]. In *syn*-2,3;4,5-diepoxy-12-oxa[4.4.3]propellane the tetrahydrofuran ring has a mirror plane (Table 9). However, the φ value shows that the flap of the envelope is at C(1) (notation of the original paper) and not at O(1); the torsion angle of $-34{\cdot}1°$ about the conjoining bond can thus be reconciled with the envelope conformation of the tetrahydrofuran ring.

In *anti*-2,3;4,5-diepoxy-12-oxa[4.4.3]propellane (Kaftory, 1980*b*) both independent molecules in the asymmetric unit have twist conformations for the five-membered rings, distorted so that they are about $\frac{1}{3}$ of the way along the path to the envelope conformation (but in opposite directions). Thus Kaftory's statement that the five-membered rings of the two independent molecules of the *anti* isomer (DIDN in his notation) have envelope conformations is wrong; the non-mixing corollary is obeyed for this compound.

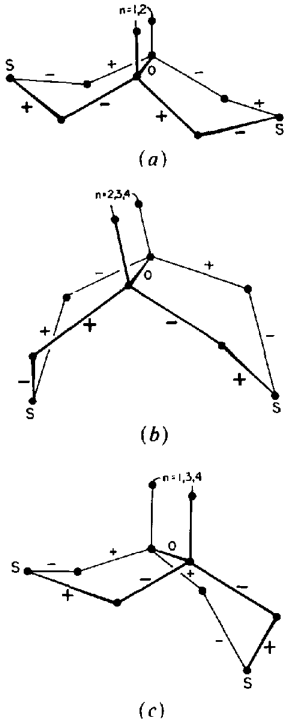
Various conformations are found for the propellane(ene) moiety *as a whole* within the framework of the 'non-mixing' restriction. We consider first the examples where the rings have m symmetry and thus the propellane(ene) moieties are achiral. For $n = 1$ and 2, two different overall symmetries are found. In the first *kind* the propellane moiety has C_{2v} ($mm2$) symmetry but there are two subdivisions. In the first of these there is an *anti,anti* arrangement of thiolane rings with respect to the aliphatic ring in the cation of the Pd salt (Fig. 27*b*). The $PdCl_2$ complex and the Pd salt with dithia[3.3.3]propellane also belong to this group. The second subdivision is *syn,syn* which is found in the bis(iodine) and $HgCl_2$ complexes (Figs. 26*b* and 26*c*). The second *kind* of propellane moiety has m symmetry and is *syn,anti*; this conformation is found in dithia[3.3.1]propellane disulfoxide (Fig. 26*d*). The oxygens in the disulfoxide are linked *axial,axial* in the major component of the mixed crystal and *equatorial,axial* in the minor component. Dithia[3.3.3]propellane as free molecule and in its

$HgCl_2$ complex has the *syn,anti* structure (Figs. 28*a*, *b*); this has quasi 3/*m* symmetry if the difference between S and CH_2 is ignored while its symmetry is *m* if this difference is taken into account. Oxathia[4.3.3]propellane.$HgCl_2$ is isostructural with dithia[3.3.3]propellane.$HgCl_2$ and has the same overall conformation.

Each overall conformation has its own characteristic pattern of *signs* of torsion angles (Fig. 38); torsion angles in the aliphatic ring are not included in this discussion. The sign patterns of the *anti,anti* and *syn,syn* conformations are enantiomerically related, the point-group symmetry of the torsion-angle sign pattern (*not* of the atomic arrangement) being 2. The sign pattern of the *syn,anti* arrangement has symmetry *m*.

Thus, to summarize, there are three possible arrangements in a propellane(ene) moiety containing thiolane rings with *m* symmetry; all three have been encountered during this study. The first and third arrangements (Figs. 38*a* and 38*c*) occur in the neat molecules or where complexation (or formation of the sulfoxide) appears not to affect the overall conformation; however, the second arrangement (Fig. 38*b*) occurs only in palladium compounds and appears to be a consequence of the complexation geometry imposed by the palladium.

We now turn to molecules in which the thiolane rings have 2 symmetry, the third ring being cyclohexene (Figs. 31*a*–*e*). If the distinction between –CH=CH– and –S is ignored then the propellene moieties have D_3 (32) symmetry but their true symmetry is C_1 (1). Thus these propellenes are chiral. In bis(dithia[4.3.3]propellene).$CdCl_2$ the two propellene moieties linked to a particular Cd^{2+} have the same chirality. Spontaneous resolution on crystallization has been encountered only for the neat crystals of dithia[4.3.3]propellene disulfoxide. In dithia-[4.3.3]propellene.$HgCl_2$ one S is linked to Hg by an *anti* lone pair and the other by a *syn* lone pair, while the linkages to oxygen are *anti,anti* in dithia[4.3.3]propellene disulfoxide as found in the monohydrate. In the $CdCl_2$ complex one propellene moiety is linked to Cd^{2+} *via* an *anti* and the other *via* a *syn* lone pair; in the (oxathia[4.3.3]propellene)$_2$.$PdCl_2$ the S···Pd link is *via* a *syn* lone pair (Fig. 14). [4.4.4]Propellatriene (Ermer, Gerdil & Dunitz, 1971) has very nearly D_3 (32) symmetry in its crystals. The saturated analogues [4.4.4]propellane (Ermer, Gerdil & Dunitz, 1971) and 2,10,11-trioxatricyclo[4.4.4.0^{1,6}]tetradecane (Banyard & Dunitz, 1976) have similar staggered overall conformations, with approximate D_3 and C_3 symmetries, respectively, and rings in the chair conformation.



(*a*)

(*b*)

(*c*)

Fig. 38. Patterns of *signs* of torsion angles in thiolane rings of propellane(ene) moieties.

(4) *Molecular complexes of the dithia(and oxathia)[n.3.3] propellanes(enes)*

(i) *The mercuric chloride complexes*. The mercuric chloride complex of thiolane has been prepared (Grischkewitsch-Trokhimovskii, 1916; Mozingo, Harris, Wolf, Hoffhine, Easton & Folkers, 1945) but its structure has not been reported. All except one of the present complexes are of known types. We discuss them in order of descending Hg coordination number.

(*a*) Six-coordination (4S+2Cl). Sheets of $HgCl_2$ molecules and S atoms of thiolane rings are formed in the structure of dithia[3.3.1]propellane.$HgCl_2$, with the Hg–Cl vectors approximately normal to the planes containing the Hg and S atoms (Fig. 5). The $HgCl_2$ molecules are only slightly distorted from linearity (the free molecules are linear). The S atoms are symmetrically located in the sheets with respect to the Hg atoms. Similar structures do not appear to have been reported. The closest analogue is bis(biuret).$HgCl_2$ (Birker, Freeman, Guss & Watson, 1977) where the $HgCl_2$ molecules are hardly perturbed and are normal to ribbons containing pseudo-octahedral Hg atoms bridged by bicoordinate oxygen atoms of four different biuret molecules. The biuret ligands are monodentate but each coordinating oxygen is unsymmetrically linked to two Hg atoms [d(Hg–Cl) = 2·30, d(Hg···O) = 2·76, 2·95 Å].

Ribbon structures rather similar to those described are well known among $HgCl_2$ complexes; in the more usual type, exemplified by (phenoxathiin)$_2$.$HgCl_2$ (Cheung, McEwen & Sim, 1965), the ribbons contain $HgCl_2$ molecules linked by weak Hg···Cl interactions, the Hg–S vectors being approximately normal to the plane of the ribbon. Thus there are appreciable differences from the arrangement found in dithia[3.3.1]propellane.$HgCl_2$. The balance appears to be a delicate one since bis(biuret).$HgCl_2$ crystallizes in a second form with Cl bridging between Hg atoms (Nardelli & Chierici, 1960).

(*b*) Four-coordination (2S+2Cl). Two types of arrangement can be distinguished. In the first, discrete dimers are formed, as in the essentially similar arrangements in dithia[3.3.3]propellane.$HgCl_2$ and oxathia[4.3.3]propellene.$HgCl_2$ (Figs. 6 and 8). The same structural arrangement is found in 1-methylcytosine.$HgCl_2$ (Authier-Martin & Beauchamp, 1977).

In the second type of complex, exemplified here by dithia[4.3.3]propellene.$HgCl_2$ (Fig. 7), there is a polymeric arrangement in which distorted $HgCl_2$ molecules link between two sulfurs of different dithia[4.3.3]propellene molecules. On either side the chain is continued by similar S···Hg links involving the second sulfur of each propellene moiety. A similar polymeric arrangement is found in 1,3,5-trithian.$HgCl_2$ (Costello, McPhail & Sim, 1966) while bis(1,4-dithioxan).$HgCl_2$ (McEwen & Sim, 1967) is a discrete-molecule analogue.

(ii) *The bis(diiodine) molecular complexes.* The dithia[3.3.1]- and dithia[3.3.2]propellane complexes have very similar molecular structures, with the same kind of linkage of I_2 to S in both compounds. Many charge-transfer compounds containing S···I secondary interactions are known (Hassel, 1972; Herbstein & Schwotzer, 1984); we compare our present results to one typical structure, the centrosymmetric 1,4-dithiane.$2I_2$ compound (Chao & McCullough, 1960), where the S···I links are equatorial. The S···I and I–I distances are compared in Table 10; as expected, the S···I distances are shortened with respect to the sum of the van der Waals radii (1·80+2·10=3·90 Å) while *d*(I–I) is increased over the gas-phase [2·667 (2) Å] and solid-phase [2·715 (6) Å] values. Our present values fit well on the plot of *d*(S···I) against *d*(I–I) given by Herbstein & Schwotzer (1984), in the region of minimum perturbation. Charge transfer is much more marked in thiolane.Br_2 (Allegra, Wilson, Benedetti, Pedone & Albert, 1970), where the principal contributor to the resonance hybrid is the ionic structure $C_4H_8S^+.Br^-$, than in the dithia[3.3.*n*]propellane.$2I_2$ molecular compounds.

The dithia[3.3.1]propellane.$2I_2$ crystal structure contains paired complex units that can be represented schematically as:

$$\mathrm{I(4)–I(3)\cdots S(2)C_7H_{10}S(1)\cdots I(1)–I(2)\ \bar{1}\ I(2')–I(1')}$$
$$\mathrm{\cdots S(1)C_7H_{10}S(2')\cdots I(3')–I(4').}$$

The I(2)···I(2′) distance of 3·720 (1) Å across the centre of symmetry is appreciably smaller than the van der Waals distance; the angle I(1)–I(2)···I(2′) is 154·2 (1)° so that the interaction deviates significantly from linearity. Linear I_4^{2-} ions are well known (see summary in Herbstein, Kapon & Schwotzer, 1983) but have the approximate structure $I^-\cdots I_2\cdots I^-$, quite different from the $I_2\cdots I_2$ arrangement found here. It is somewhat surprising that the $I_2\cdots I_2$ secondary interaction has no obvious effect on *d*(S···I) or *d*(I–I).

Table 10. *Comparison of d*(S···I) *and d*(I···I) *for three compounds*

Compound	*d*(S···I) (Å)	*d*(I···I) (Å)	Reference
1,4-Dithiane.$2I_2$	2·867 (6)	2·787 (2)	Chao & McCullough (1960)
Dithia[3.3.1]propellane.$2I_2$	2·852 (2) 2·806 (2)	2·797 (1) 2·796 (1)	Present work
Dithia[3.3.2]propellane.$2I_2$	2·803 (2) 2·902 (2)	2·794 (1) 2·767 (1)	Present work
Sum of van der Waals radii	3·9	4·2	
Sum of covalent radii	2·34	2·67	

(iii) *The* $CdCl_2$ *complex.* Bis(dithia[4.3.3]propellene).$CdCl_2$ (Fig. 9) has twisted chains in which Cl atoms bridge between Cd atoms; there is approximate octahedral coordination about Cd and two propellene moieties are *cis* linked to a particular Cd. The second S atom of a propellene does not have secondary links to other atoms. The two Cd···Cl interactions within the bridges are of similar strengths {*d*[Cd–Cl(1)]= 2·590 (2), *d*[Cd–Cl(2)]=2·622 (2) Å}. The various Cd–S distances are essentially equal at 2·82 Å. Similar dimensions are found in the related, discrete-molecule structure of di-μ-chloro-dichlorobis(6-mercaptopurine)diaquacadmium(II) (Griffith & Amma, 1979). Here the bridging Cd–Cl distances are 2·60, 2·63 Å while the non-bridging Cd–Cl distance is 2·49 Å and *d*(Cd–S) is 2·79 Å (e.s.d.'s 0·003 Å). There is distorted octahedral coordination about Cd^{2+}. The unique Cd–Cl distance is appropriate for a normal single bond, but the Cd–S distances are appreciably elongated with respect to the normal single-bond value (2·52 Å), as are the bridging Cd–Cl distances.

These various Cd–S distances are appreciably longer than the distances found between octahedral Cd and thione S [2·58–2·65 Å, according to the summary of Bigoli, Leporati & Pellinghelli (1976*a*)], which are in turn larger than the corresponding values found when Cd is tetrahedrally coordinated [~2·50 Å (Bigoli, Leporati & Pellinghelli, 1976*b*)].

The present polymeric arrangement is remarkably similar to those found in the *anion* chains of pyridinium tetrachloroantimonate(III) (Porter & Jacobson, 1970) and pyridinium tetrabromoantimonate(III) (DeHaven & Jacobson, 1976). There are direct resemblances in the twisted nature of the chains, the unsymmetrical halogen bridges and the two *cis*-located unique moieties [propellene moieties for the $CdCl_2$ complexes and halogen atoms for the tetrahaloantimonate(III) chains].

(iv) *Complexes with* $PdCl_2$. Three types of complex can be distinguished:

(*a*) *cis*-(2S+2Cl) coordination. Here a *cis*-dichloropalladium(II) moiety interacts with two S atoms of thiolane rings in the same propellane(ene) molecule. The resulting complex is neutral. Two examples were encountered: dithia[3.3.3]propellane.$PdCl_2$ and dithia[4.3.3]propellene.$PdCl_2$. Nitrogen analogues, $R.PdCl_2$, have been reported with R = 7,10-dimethyl-7,10-diaza[3.3.3]propellan-3-one and 8,11-dimethyl-8,11-diaza[4.3.3]propellane (and 'ene') (Korat, Schmuckler & Ginsburg, 1970).

(*b*) 4S coordination about Pd. The examples found were{bis(dithia[*n*.3.3]propellane)palladium(II)}Cl_2.-$4H_2O$ ($n = 2, 3$) where Pd^{2+} interacts with four S atoms from two dithia[*n*.3.3]propellane molecules giving cations. Neutral complexes of this type are also known (Table 11).

(*c*) *trans*-(2S+2Cl) coordination. These are *trans*-dichloropalladium(II) complexes where Pd interacts with two S atoms of different molecules. The ligand was oxathia[4.3.3]propellene in the only example encountered here. This is a molecular structure. It appears that oxygen does not interact with Pd in the same way as S and thus formation of (*a*) or (*b*) types is ruled out.

The complexes are all square planar with bond angles close to 90°. The complexes of type (*b*) show quasi-octahedral 4+2 coordination about Pd, the axial sites being occupied by remote Cl^- ions $\{d(Pd\cdots Cl^-) = 3{\cdot}446\,(1)$ Å for the [3.3.2] cation and $3{\cdot}348\,(1)$ Å for the [3.3.3] cation$\}$.

Values of d(Pd–Cl) and d(Pd–S) are summarized in Table 11. The evidence for a *trans* influence* on d(Pd–Cl) has been given by Alléaume, Gulko, Herbstein, Kapon & Marsh (1976). The present, and other, results demonstrate a similar *trans* influence for d(Pd–S). When Cl is *trans* to S, $d(Pd–S) \sim 2{\cdot}27$ Å, while, for S *trans* to S, $d(Pd–S) \sim 2{\cdot}33$ Å.

Table 11. *Values* (Å) *of* d(Pd–Cl) *and* d(Pd–S) *in various palladium chloride complexes*

Type (*a*)

Complex	d(Pd–Cl) *trans* to S	d(Pd–S) *trans* to Cl	Reference
(1) Dithia[3.3.3]propellane.$PdCl_2$	2·321 (2) 2·336 (2)	2·280 (2) 2·272 (2)	(*a*)
(2) Dithia[4.3.3]propellene.$PdCl_2$	2·324 (2) 2·340 (2)	2·286 (2) 2·281 (2)	(*a*)
(3) *cis*-Dichloro(D,L-methionine)Pd	2·332 (4)	2·265 (4)	(*b*)
(4) *cis*-Dichloro(*S*-methyl-L-cysteine)palladium(II) monohydrate	2·324 (3) 2·312 (7)	2·230 (4) 2·261 (4)	(*c*)
(5) *cis*-Dichloro(diaza-1,10-tetraoxa-4,7,13,16-dithia-21,24-bicyclo[8.8.8]hexacosane)palladium(II)	2·301 (1) 2·305 (2)	2·265 (4) 2·264 (1)	(*d*)
(6) *cis*-Dichloro(*O*-methyl-*N*-allylthiocarbamato)palladium(II)	2·327 (7)	2·295 (6)	(*e*)
Mean	2·322 (13)	2·270 (17)	

Type (*b*)

Complex	d(Pd–S) *trans* to S	Reference
(1) {Bis(dithia[3.3.2]propellane)palladium(II)}$Cl_2.4H_2O$	2·346 (1) 2·329 (1)	(*a*)
(2) {Bis(dithia[3.3.3]propellane)palladium(II)}$Cl_2.4H_2O$	2·335 (1) 2·326 (1)	(*a*)
(3) Tetrakis(thiourea)palladium(II) chloride (monoclinic form)	2·33 (-) 2·35 (-)	(*f*)
(4) Tetrakis(thiourea)palladium(II) chloride (orthorhombic form)	2·315 (4) 2·330 (4) 2·341 (4) 2·346 (4)	(*g*)
(5) Bis(*N*,*N*-diethyldithiocarbamato)palladium(II)	2·317 (3) 2·315 (3)	(*h*)
(6) Bis(dimethyl-*o*-thiolophenylarsine)palladium(II)	2·296 (19)	(*i*)
(7) Bis{[*O*,*O*'-bis(2,6-dimethylphenyl)dithiophosphato]-*S*,*S*'}palladium(II)	2·346 (1) 2·344 (1)	(*j*)
Mean	2·332 (17)	

Type (*c*)

Complex	d(Pd–Cl) *trans* to Cl	d(Pd–S) *trans* to S	Reference
(1) Bis(oxathia[4.3.3]propellene).$PdCl_2$	2·296 (1)	2·322 (1)	(*a*)
(2) Dichlorobis(thiomorpholine)-palladium(II)	2·313 (1)	—	(*k*)

References: (*a*) this work; (*b*) Warren, McConnell & Stephenson (1970); (*c*) Battaglia, Bonamartini Corradi, Grasselli Palmieri, Nardelli & Vidoni Tani (1973); (*d*) Louis, Thierry & Weiss (1974); (*e*) Porta (1971); (*f*) Ooi, Kawase, Nakatsu & Kuroya (1960); (*g*) Berta, Spofford, Boldrini & Amma (1970); (*h*) Beurskens, Cras, Hummelink & Noordik (1971); (*i*) Beale & Stephenson (1972); (*j*) Roques, Blonski, Klaebe, Perie, Declercq & Germain (1981); (*k*) Fowler & Griffiths (1978) - note that the ligand is bonded to Pd *via* N, not S.

(5) *The* $Cl^-\cdots H_2O$ *networks*

The $[(H_2O)_4(Cl^-)_2].[(H_2O)_2(Cl^-)_2]$ hydrogen-bonded ribbons found in the crystals of {bis(dithia-[*n*.3.3]propellane)palladium(II)}$Cl_2.4H_2O$ ($n = 2, 3$) [§ III(xv)] appear to be novel, although similar $(H_2O)_6(H_2O)_4$ ribbons have recently been found in bis(tetrahydropicolinato)copper(II) octahydrate (Kapon, 1986). A somewhat analogous arrangement has been reported in 2,3,3a,4,5,6-hexahydro-8-methyl-1*H*-pyrazino[3,2,1-*j*,*k*]carbazole hydrochloride dihydrate (pyrazidole; Karapetyan, Struchkov & Dvoryantseva, 1982). The Cl^- : H_2O ratio is 1 : 2, as in the present salts, and ribbons of hydrogen-bonded water molecules and Cl^- ions can be identified (Fig. 39). However, there are definite differences. Firstly the present arrangement is one-dimensional (ribbons) whereas in pyridazole (as noted by Karapetyan *et al.*) the ribbons are linked into sheets to give a two-dimensional arrangement. Furthermore, here we find $2H_2O+2Cl^-$ in four-membered rings and $4H_2O+2Cl^-$ in six-membered rings whereas pyridazole has $4H_2O$ in four-membered and $8H_2O+4Cl^-$ in twelve-membered rings; the Cl^- ions are three-coordinate both here (linked to three water molecules) and in pyridazole (two water

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* The *trans* influence of a ligand in a metal complex is the extent to which that ligand weakens the bond *trans* to itself in the equilibrium state of that complex. The *trans* effect is the effect of a coordinated group *A* upon the rate of the substitution reaction of the group opposite to *A*. Thus the *trans* influence depends on thermodynamic factors and the *trans* effect on kinetic factors; this distinction was first introduced by Pidcock, Richards & Venanzi (1966).

Table 12. *Atomic parameters for non-hydrogen atoms (coordinates for* Hg, I, Cd, Pd × 10^5 *and other coordinates* × 10^4*)*

$U_{eq}=\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ (Å^2 × 10^4). Standard deviations are in parentheses in units of the last significant figure; $\sigma(U_{eq})$ is calculated according to Schomaker & Marsh (1983). The omission of an e.s.d. denotes an atom at a special position. Values marked with a dagger are U_{iso}.

(i) Dithia[3.3.1]propellane

	x	*y*	*z*	U_{eq}
S(1*A*)‡	−2801	2807 (1)	6941	685 (7)
S(2*A*)	767 (7)	3562 (1)	3524 (7)	713 (7)
C(1*A*)	−1873 (14)	3099 (2)	3882 (14)	460 (17)
C(2*A*)	−3947 (18)	3005 (3)	4100 (19)	633 (25)
C(3*A*)	64 (19)	3002 (3)	8184 (22)	648 (27)
C(4*A*)	362 (14)	3096 (2)	6123 (14)	446 (17)
C(5*A*)	1858 (20)	3382 (2)	6410 (18)	626 (25)
C(6*A*)	−2095 (18)	3381 (2)	2296 (17)	540 (20)
C(7*A*)	−68 (17)	2845 (2)	4314 (17)	546 (21)
S(1*B*)	640 (7)	4690 (1)	3829 (7)	691 (7)
S(2*B*)	7633 (6)	3938 (1)	7263 (7)	714 (7)
C(1*B*)	4645 (13)	4405 (2)	6938 (13)	460 (17)
C(2*B*)	2319 (18)	4500 (2)	6644 (18)	586 (25)
C(3*B*)	2302 (19)	4501 (2)	2632 (18)	597 (24)
C(4*B*)	4590 (14)	4403 (2)	4624 (13)	454 (17)
C(5*B*)	5812 (21)	4110 (3)	4370 (18)	601 (26)
C(6*B*)	5933 (18)	4116 (2)	8401 (16)	561 (22)
C(7*B*)	5994 (17)	4651 (2)	6428 (17)	567 (22)

‡ *x*, *z* held constant to define origin.

(ii) Dithia[3.3.3]propellane

	x	*y*	*z*	U_{eq}
S(1)	619 (1)	241 (1)	2430 (2)	610 (3)
S(2)	1294 (1)	3843 (1)	551 (1)	654 (3)
C(1)	−112 (3)	2466 (3)	2341 (4)	377 (7)
C(2)	−614 (3)	1223 (3)	2325 (5)	479 (8)
C(3)	1389 (3)	1179 (3)	4116 (6)	536 (9)
C(4)	1134 (3)	2446 (3)	3451 (4)	406 (7)
C(5)	2032 (3)	2837 (4)	2166 (6)	569 (9)
C(6)	30 (3)	2888 (3)	390 (5)	504 (9)
C(7)	−835 (3)	3326 (3)	3417 (5)	475 (8)
C(8)	−257 (3)	3294 (3)	5386 (5)	495 (8)
C(9)	1043 (3)	3283 (3)	5085 (5)	513 (9)

(iii) Dithia[4.3.3]propellene

	x	*y*	*z*	U_{eq}
S(1*A*)	2740 (2)	9404 (1)	5383 (1)	712 (4)
S(2*A*)′	−316 (6)	7749 (1)	4857 (3)	709 (13)
S(2*A*)″	−1519 (19)	8811 (7)	7783 (8)	1389 (67)
C(1*A*)	−525 (6)	8802 (2)	5757 (3)	406 (10)
C(2*A*)	395 (7)	9143 (2)	4870 (4)	557 (13)
C(3*A*)	2704 (6)	8944 (2)	6545 (4)	596 (13)
C(4*A*)	1144 (6)	8485 (2)	6335 (3)	436 (11)
C(5*A*)	1859 (8)	8017 (2)	5598 (5)	799 (17)
C(6*A*)	−1921 (7)	8339 (2)	5319 (4)	648 (14)
C(7*A*)	−1552 (6)	9216 (2)	6512 (4)	528 (12)
C(10*A*)	460 (8)	8213 (2)	7365 (4)	640 (14)
S(1*B*)	−1842 (2)	5424 (1)	7089 (1)	814 (5)
S(2*B*)′	−5135 (7)	7038 (2)	7789 (3)	840 (12)
S(2*B*)″	−6471 (10)	6013 (4)	4750 (5)	715 (17)
C(1*B*)	−5279 (6)	5971 (2)	6851 (4)	540 (12)
C(2*B*)	−4136 (9)	5620 (2)	7678 (4)	831 (17)
C(3*B*)	−2188 (7)	5908 (2)	5977 (4)	670 (16)
C(4*B*)	−3797 (6)	6328 (2)	6258 (3)	488 (12)
C(5*B*)	−3048 (8)	6794 (2)	7016 (5)	791 (17)
C(6*B*)	−6659 (8)	6396 (4)	7378 (5)	918 (21)
C(7*B*)	−6296 (8)	5550 (3)	6064 (6)	1069 (24)
C(10*B*)	−4712 (9)	6610 (3)	5292 (4)	870 (18)
C(8*A*)′	−1933 (52)	9003 (14)	7605 (26)	677 (62)†
C(9*A*)′	−787 (21)	8524 (6)	7966 (14)	590 (40)†
C(8*A*)″	−1082 (21)	7835 (8)	4776 (15)	276 (44)†
C(9*A*)″	432 (24)	7663 (8)	5085 (14)	368 (52)†
C(8*B*)′	−6094 (17)	5789 (5)	5051 (10)	851 (44)†
C(9*B*)′	−5996 (18)	6317 (5)	4664 (10)	910 (42)†
C(8*B*)″	−6034 (38)	6856 (13)	7796 (24)	694 (89)†
C(9*B*)″	−4337 (49)	7070 (18)	7510 (28)	776 (**)†

(iv) Dithia[3.3.1]propellane.$HgCl_2$

	x	*y*	*z*	U_{eq}
Hg	75000	25000	2427 (14)	460 (3)
Cl	9367 (3)	2500	−117 (6)	528 (10)
S(1)	7500	4600 (4)	4954 (4)	324 (7)
C(1)	6893 (6)	7500	3854 (17)	257 (18)
C(2)	6407 (8)	6000 (11)	4773 (15)	359 (18)
C(7)	7500	7500	1220 (26)	372 (35)

(v) Dithia[3.3.3]propellane.$HgCl_2$

	x	*y*	*z*	U_{eq}
Hg	51686 (5)	53684 (3)	71229 (10)	524 (2)
Cl(1)	5294 (3)	6854 (4)	4672 (5)	469 (10)
Cl(2)	6704 (3)	4933 (5)	7827 (6)	529 (11)
S(1)	3582 (3)	5867 (4)	7925 (5)	371 (9)
S(2)	583 (3)	6248 (5)	8594 (5)	447 (10)
C(1)	1922 (10)	5789 (14)	6627 (17)	281 (35)
C(2)	2941 (11)	6182 (15)	6240 (19)	376 (40)
C(3)	2994 (11)	4220 (16)	8115 (17)	350 (38)
C(4)	1953 (10)	4573 (15)	7778 (17)	303 (33)
C(5)	1486 (12)	5056 (15)	9243 (19)	385 (39)
C(6)	1414 (11)	6980 (15)	7333 (18)	354 (39)
C(7)	1396 (12)	5199 (16)	5288 (20)	377 (39)
C(8)	1533 (12)	3631 (17)	5405 (20)	432 (44)
C(9)	1464 (12)	3359 (15)	7026 (19)	405 (43)

(vi) Dithia[4.3.3]propellene.$HgCl_2$

	x	*y*	*z*	U_{eq}
Hg	−6870 (5)	−21232 (10)	101725 (10)	345 (1)
Cl(1)	−1453 (3)	827 (3)	11168 (4)	408 (7)
Cl(2)	829 (2)	−2987 (4)	12336 (4)	391 (6)
S(1)	−848 (2)	−3377 (3)	6405 (3)	244 (5)
S(2)	−2654 (2)	−3298 (3)	537 (4)	302 (6)
C(1)	−2804 (9)	−4139 (11)	3483 (14)	256 (22)
C(2)	−2142 (9)	−4740 (13)	5100 (15)	286 (22)
C(3)	−1473 (10)	−1713 (12)	5538 (14)	301 (24)
C(4)	−2740 (9)	−2172 (12)	4475 (15)	275 (22)
C(5)	−3110 (9)	−1597 (14)	2734 (16)	326 (24)
C(6)	−2168 (10)	−4747 (12)	1753 (13)	303 (25)
C(7)	−4039 (10)	−4782 (16)	2706 (18)	408 (28)
C(8)	−4893 (10)	−3694 (20)	3895 (22)	456 (39)
C(9)	−4690 (11)	−2157 (19)	5378 (24)	480 (37)
C(10)	−3500 (10)	−1327 (15)	6028 (18)	373 (26)

(vii) Oxathia[4.3.3]propellene.$HgCl_2$

	x	*y*	*z*	U_{eq}
Hg	−1049 (6)	−1650 (10)	27185 (10)	497 (2)
Cl(1)	−1587 (3)	233 (4)	1751 (4)	413 (8)
Cl(2)	256 (3)	1958 (4)	4865 (4)	399 (8)
S(1)	1447 (2)	−695 (4)	2282 (4)	296 (7)
O(1)	3274 (7)	1573 (10)	5285 (10)	377 (25)
C(1)	3036 (8)	572 (11)	2760 (14)	210 (28)
C(2)	2075 (9)	972 (13)	2189 (15)	305 (28)
C(3)	1986 (8)	−947 (14)	4208 (13)	277 (26)
C(4)	2978 (8)	−618 (12)	4034 (13)	191 (23)
C(5)	3441 (12)	75 (13)	5503 (15)	377 (36)
C(6)	3481 (10)	1803 (13)	3749 (15)	305 (31)
C(7)	3577 (10)	150 (13)	1447 (15)	305 (30)
C(8)	4399 (9)	−674 (14)	1952 (16)	336 (30)
C(9)	4354 (10)	−1719 (15)	2989 (17)	392 (32)
C(10)	3507 (9)	−1980 (12)	3645 (14)	291 (31)

(viii) Bis(dithia[4.3.3]propellene).$CdCl_2$

	x	*y*	*z*	U_{eq}
Cd	25874 (6)	48983 (2)	6493 (4)	307 (1)
Cl(1)	−484 (2)	4368 (1)	129 (1)	370 (4)
Cl(2)	5965 (2)	5287 (1)	1213 (1)	395 (4)
S(1*A*)	4069 (3)	4109 (1)	2005 (2)	449 (5)
S(2*A*)	7174 (4)	2703 (1)	2280 (3)	887 (8)
C(1*A*)	4905 (10)	3301 (2)	882 (6)	434 (18)
C(2*A*)	5815 (10)	3780 (3)	1295 (8)	641 (26)
C(3*A*)	2478 (10)	3583 (2)	2015 (6)	478 (19)
C(4*A*)	3681 (9)	3138 (2)	1773 (6)	375 (17)
C(5*A*)	5101 (13)	2995 (3)	2796 (7)	678 (25)
C(6*A*)	6456 (12)	2904 (3)	841 (8)	725 (27)
C(7*A*)	3676 (13)	3367 (3)	−272 (7)	651 (25)
C(8*A*)	2057 (17)	2997 (4)	−522 (8)	753 (31)
C(9*A*)	1534 (14)	2740 (4)	153 (12)	882 (40)
C(10*A*)	2414 (12)	2707 (3)	1344 (9)	695 (31)
S(1*B*)	1342 (2)	5112 (1)	2739 (1)	345 (4)
S(2*B*)	5431 (3)	6375 (1)	3497 (2)	513 (5)
C(1*B*)	3066 (8)	5723 (2)	4328 (5)	279 (14)
C(2*B*)	3523 (9)	5275 (2)	3666 (5)	325 (15)
C(3*B*)	236 (8)	5709 (2)	2866 (5)	344 (16)
C(4*B*)	1789 (8)	6044 (2)	3463 (5)	316 (15)
C(5*B*)	3101 (10)	6246 (2)	2663 (6)	417 (17)
C(6*B*)	4901 (9)	6020 (3)	4690 (6)	454 (18)
C(7*B*)	2043 (9)	5573 (2)	5339 (5)	379 (16)
C(8*B*)	788 (10)	5967 (3)	5710 (6)	490 (19)
C(9*B*)	281 (10)	6356 (3)	5135 (6)	481 (20)
C(10*B*)	867 (9)	6479 (2)	4021 (6)	385 (17)

Table 12 (*cont.*)

	x	y	z	U_{eq}
(ix) Dithia[3.3.1]propellane.$2I_2$				
I(1)	20824 (6)	35786 (7)	−20577 (9)	347 (2)
I(2)	5542 (7)	17657 (10)	−42344 (10)	440 (2)
I(3)	32175 (6)	106869 (7)	35561 (9)	324 (2)
I(4)	47252 (6)	125627 (9)	56734 (11)	435 (2)
S(1)	3560 (2)	5273 (3)	320 (4)	352 (5)
S(2)	1726 (2)	8997 (3)	1214 (4)	353 (5)
C(1)	2612 (8)	7717 (9)	−443 (12)	301 (17)
C(2)	3636 (10)	7414 (11)	−968 (15)	407 (23)
C(3)	2488 (9)	4925 (9)	1886 (12)	327 (20)
C(4)	1962 (7)	6335 (9)	1092 (11)	267 (16)
C(5)	1688 (9)	6883 (11)	2452 (14)	313 (20)
C(6)	2815 (9)	9306 (11)	−309 (14)	357 (22)
C(7)	1321 (8)	6756 (11)	−853 (12)	347 (19)
(x) Dithia[3.3.2]propellane.$2I_2$				
I(1)	−22642 (8)	15235 (3)	105023 (6)	437 (2)
I(2)	−41241 (10)	23225 (4)	115355 (9)	619 (2)
I(3)	29909 (8)	11107 (3)	40279 (6)	425 (2)
I(4)	48597 (8)	4195 (3)	28195 (8)	522 (2)
S(1)	−214 (3)	850 (1)	9391 (3)	449 (6)
S(2)	885 (3)	1842 (1)	5130 (3)	464 (6)
C(1)	1495 (10)	1364 (4)	7919 (9)	350 (18)
C(2)	1216 (14)	1467 (4)	9369 (11)	399 (22)
C(3)	−1486 (14)	899 (6)	7285 (12)	530 (26)
C(4)	−115 (10)	1007 (4)	6670 (9)	357 (18)
C(5)	−872 (14)	1357 (5)	5117 (11)	505 (24)
C(6)	1842 (16)	1950 (5)	7214 (11)	507 (27)
C(7)	2682 (15)	820 (6)	7991 (14)	493 (26)
C(8)	1136 (15)	454 (5)	6817 (12)	488 (27)
(xi) Dithia[3.3.3]propellane.$PdCl_2$				
Pd	44090 (5)	25000	−3500 (5)	325 (2)
Cl(1)	5928 (2)	2500	568 (2)	434 (5)
Cl(2)	3570 (2)	2500	1381 (2)	393 (5)
S(1)	2908 (2)	2500	−1249 (2)	371 (5)
S(2)	5306 (2)	2500	−1978 (2)	426 (6)
C(3)	2965 (5)	787 (10)	−2350 (5)	388 (15)
C(4)	3729 (4)	1405 (8)	−3225 (5)	324 (12)
C(5)	4773 (5)	788 (11)	−2885 (6)	424 (16)
C(8)	3813 (9)	2500	−5160 (9)	539 (29)
C(9)	3482 (6)	922 (10)	−4451 (6)	416 (15)
(xii) Dithia[4.3.3]propellene.$PdCl_2$				
Pd	45112 (4)	25000	−5329 (6)	326 (2)
Cl(1)	5826 (2)	2500	601 (2)	408 (6)
Cl(2)	5411 (2)	2500	−2174 (2)	451 (6)
S(1)	3220 (2)	2500	−1657 (2)	383 (6)
S(2)	3698 (2)	2500	1115 (2)	414 (7)
C(1)	2114 (4)	1442 (8)	69 (5)	290 (13)
C(2)	2432 (5)	810 (9)	−1097 (5)	326 (14)
C(6)	2806 (5)	821 (10)	967 (5)	347 (15)
C(7)	1135 (5)	658 (11)	323 (6)	390 (16)
C(8)	700 (5)	1609 (11)	1306 (6)	490 (19)
(xiii) Bis(oxathia[4.3.3]propellene).$PdCl_2$				
Pd	0	0	0	371 (2)
Cl	−1641 (2)	318 (2)	−799 (1)	597 (3)
S(1)	−368 (2)	−1957 (1)	−85 (1)	510 (4)
O(1)	843 (5)	−4997 (4)	−1110 (4)	753 (18)
C(1)	1211 (5)	−3009 (5)	−1079 (4)	402 (14)
C(2)	985 (8)	−2795 (6)	−166 (5)	561 (21)
C(3)	−859 (7)	−2328 (7)	−1123 (6)	603 (23)
C(4)	−2 (6)	−3206 (5)	−1473 (4)	492 (16)
C(5)	−265 (8)	−4423 (7)	−1175 (8)	728 (29)
C(6)	1783 (7)	−4185 (6)	−1184 (6)	591 (21)
C(7)	1921 (8)	−2012 (7)	−1442 (6)	638 (24)
C(8)	1706 (11)	−1762 (8)	−2282 (7)	897 (34)
C(9)	856 (15)	−2253 (9)	−2723 (7)	1088 (51)
C(10)	50 (11)	−3186 (8)	−2409 (5)	790 (28)
(xiv) [Bis(dithia[3.3.2]propellane)palladium(II)]$Cl_2.4H_2O$				
Pd	0	0	0	250 (1)
Cl	−2992 (1)	2923 (1)	−352 (1)	416 (2)
S(1)	2610 (1)	1495 (1)	67 (0)	305 (2)
S(2)	−188 (1)	242 (1)	1342 (1)	301 (2)
C(1)	2043 (4)	2566 (3)	1452 (2)	271 (6)
C(2)	2121 (5)	3084 (4)	618 (2)	343 (7)
C(3)	4234 (4)	864 (4)	916 (2)	315 (7)
C(4)	3337 (4)	1198 (3)	1637 (2)	259 (6)
C(5)	2175 (5)	−65 (3)	1862 (2)	301 (7)
C(6)	65 (5)	2163 (4)	1564 (2)	341 (7)
C(7)	3296 (6)	3392 (4)	2141 (2)	396 (8)
C(8)	4547 (5)	2049 (4)	2317 (2)	388 (8)
O*W*(1)	223 (7)	−3567 (6)	1589 (2)	874 (14)
O*W*(2)	3304 (5)	4841 (4)	−1008 (2)	521 (8)
(xv) [Bis(dithia[3.3.3]propellane)palladium(II)]$Cl_2.4H_2O$				
Pd	0	0	0	253 (1)
Cl	2692 (1)	372 (2)	3197 (2)	513 (3)
S(1)	−706 (1)	2643 (1)	−565 (1)	287 (2)
S(2)	−1303 (1)	204 (1)	2450 (1)	294 (2)
C(1)	−2763 (3)	3069 (4)	1587 (5)	256 (7)
C(2)	−2544 (4)	3255 (5)	−413 (5)	316 (8)
C(3)	−368 (4)	3643 (5)	1700 (5)	299 (8)
C(4)	−1397 (4)	3316 (4)	2905 (5)	263 (7)
C(5)	−825 (4)	1835 (4)	3932 (5)	298 (8)
C(6)	−2971 (4)	1425 (5)	1798 (6)	328 (8)
C(7)	−3921 (4)	4320 (5)	2321 (6)	339 (9)
C(8)	−3385 (4)	4664 (5)	4355 (6)	388 (9)
C(9)	−1886 (4)	4709 (5)	4279 (6)	356 (9)
O*W*(1)	−4259 (5)	−1571 (5)	2890 (6)	576 (10)
O*W*(2)	−2745 (5)	−2807 (5)	−130 (9)	734 (13)
(xvi) Dithia[3.3.1]propellane disulfoxide				
S(1)	5000	−65 (1)	3701 (1)	483 (5)
S(2)	5000	3480 (1)	4398 (1)	499 (5)
O(1)‡	5000	−507 (5)	2832 (5)	601 (19)
O(1)*A*‡	5000	−789 (20)	4292 (16)	527 (66)†
O(2)	5000	2877 (5)	5212 (3)	701 (18)
C(1)	4067 (5)	1902 (3)	3392 (3)	299 (9)
C(2)	3401 (6)	910 (4)	3762 (4)	392 (13)
C(6)	3407 (6)	2926 (4)	3702 (3)	369 (11)
C(7)	5000	1872 (6)	2550 (5)	374 (15)

‡Occupation factors: O(1) 80%; O(1)*A* 20%.

	x	y	z	U_{eq}
(xvii) Dithia[4.3.3]propellene disulfoxide				
S(1)	1315 (1)	3648 (1)	3640 (1)	429 (2)
S(2)	2961 (1)	1148 (1)	7358 (1)	461 (2)
O(1)	2364 (3)	3959 (3)	2999 (5)	610 (8)
O(2)	3549 (3)	693 (4)	5793 (6)	687 (9)
C(1)	1569 (3)	3032 (3)	7063 (5)	314 (7)
C(2)	1229 (3)	4119 (3)	5914 (5)	374 (8)
C(3)	1338 (4)	1982 (4)	4242 (5)	420 (9)
C(4)	1092 (3)	1859 (3)	6205 (5)	316 (7)
C(5)	1628 (3)	747 (4)	7017 (6)	431 (9)
C(6)	2718 (3)	2811 (4)	6997 (6)	381 (8)
C(7)	1242 (3)	3181 (5)	8971 (6)	449 (9)
C(8)	138 (3)	2902 (5)	9297 (6)	503 (10)
C(9)	−431 (3)	2295 (5)	8182 (7)	554 (11)
C(10)	−71 (3)	1835 (4)	6453 (7)	467 (10)
(xviii) Dithia[4.3.3]propellene disulfoxide monohydrate				
S(1)	767 (1)	3288 (1)	1497	514 (4)
S(2)	1661 (1)	6874 (1)	−804 (2)	532 (3)
O(1)	−97 (4)	3584 (4)	395 (6)	647 (12)
O(2)	2766 (5)	7783 (4)	−576 (5)	680 (13)
C(1)	1786 (4)	5762 (4)	1517 (5)	293 (8)
C(2)	1018 (4)	4822 (4)	2347 (7)	440 (11)
C(3)	2344 (5)	3429 (5)	930 (6)	401 (13)
C(4)	2617 (4)	4894 (5)	612 (4)	281 (9)
C(5)	2225 (6)	5205 (5)	−743 (6)	426 (11)
C(6)	919 (5)	6608 (5)	699 (6)	417 (12)
C(7)	2581 (5)	6672 (5)	2385 (6)	452 (13)
C(8)	3720 (6)	5943 (7)	2906 (7)	607 (15)
C(9)	4389 (6)	5237 (7)	2156 (7)	575 (14)
C(10)	4037 (5)	5152 (6)	790 (6)	437 (12)
O*W*	−2387 (6)	4839 (6)	997 (6)	743 (13)

molecules and the NH group of the organic cations). The isolated centrosymmetric $2H_2O+2Br^-$ rings reported in 1-methyl-1,3,5,7-tetraazaadamantan-1-ium bromide hydrate (Mak, 1984) are analogous to the present $2H_2O+2Cl^-$ rings.

(6) *Summary and conclusions*

The primary factor governing the overall stereochemistry of the propellane(ene) moieties studied here is the conformation about the conjoining bond. There is either an eclipsed or a staggered conformation about this bond. Individual rings assume twist or envelope forms consistent with the central bond conformation but sometimes with appreciable deviations from ideality. Thus, in the molecules with $n = 1$, the planarity of the cyclopropane ring ensures the eclipsed arrangement about the central bond, and this holds also for $n = 2$, where puckering of the cyclobutane ring was not found. Molecular-mechanics calculations show that the eclipsed arrangement is more stable when $n = 3$ and the staggered arrangement when $n = 4$, and these calculations also predict correctly which of the propellane(ene) conformers is the most stable. The $PdCl_2$ complexes are exceptions, presumably owing to the overriding effect of the Pd···S interactions; two other exceptions among $n = 4$ molecules may result from intermolecular interactions. Thus it is only when $n = 4$ that the restrictions imposed by the moiety as a whole are sufficiently relaxed for the thiolane and aliphatic rings to take up their intrinsic lowest-energy conformations.

The 'Klammer' effect has been demonstrated; this predicts that, in the eclipsed arrangement, the angle Θ between the planes of the C atoms of the two thiolane rings will increase as n is reduced. It is found that $\Theta \sim 140°$ for $n = 1$, $\sim 124°$ for $n = 2$ and $\sim 120°$ for $n = 3, 4$. It is also found that the thiolane rings are flatter [larger values of the flap angle (Φ) of the envelope for smaller n]; thus $\Phi \sim 156°$ for $n = 1$, $\sim 141°$ for $n = 2$, $\sim 138°$ for $n = 3$ and 4. In the molecules with the smaller aliphatic rings ($n = 1, 2$) there are considerable deviations from tetrahedral bonding at the conjoining (bridgehead) carbon atoms and the 'Klammer' and ring-flattening effects derive from these distortions. The appreciable variations in the amounts of ring flattening are ascribed to crystal packing effects.

The molecular complexes are all of familiar types except for dithia[3.3.1]propellane.$HgCl_2$, where the polymeric arrangement adopted does not appear to have been encountered previously, and dithia[3.3.1]propellane.$2I_2$, where the formation of pairs of complex molecules through $I_2 \cdots I_2$ interactions has novel features.

The $Cl^- \cdots H_2O$ network found in the two Pd salt structures appears to be unique in detail although arrangements having some of its features have been reported in other crystals.

Note added in proof: Determination of thirteen additional propellane molecular structures and an extensive survey of the literature *via* the Cambridge Data File has led us to the view that there are a few molecules with overall conformations *between* eclipsed and staggered, although the great majority of molecules do belong in one or other of these categories (Herbstein, Ashkenazi, Kaftory, Kapon, Reisner & Ginsburg, 1986).

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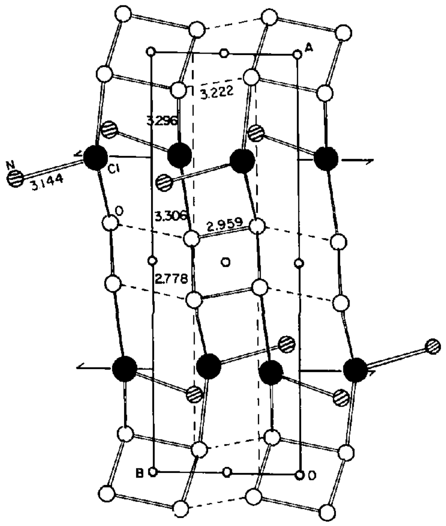

Fig. 39. Water molecule - Cl^- network in pyridazole [drawn from results of Karapetyan *et al.* (1982)]. Note that the N atoms belong to organic cations which have been omitted from the diagram.

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