Studies of Monothiomalonamide and its Palladium(II) and Platinum(II) Complexes

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A project related to the crystal engineering of hydrogen bonded coordination complexes has been initiated and our first results are presented here. The *cis* and *trans* forms of monothiomalonamide (LH_2) have been fully characterized by vibrational spectroscopy, thermal techniques and single-crystal X-ray diffraction. The *cis* form crystallizes in the monoclinic space group $P2_1/c$ and the *trans* form in the monoclinic space group $C2/c$. The respective lattice constants are $a = 5.602(3)$, $b = 9.055(2)$, $c = 10.945(5)$ Å, $\beta = 101.29(2)°$ (*cis*-LH_2) and $a = 20.336(7)$, $b = 4.317(1)$, $c = 12.432(5)$ Å, $\beta = 92.16(1)°$ (*trans*-LH_2). The new complexes $[Pd(LH_2)_4]X_2$ (X = Cl, Br), $[Pt(LH_2)_4]X_2$ (X = Br, I), $[PdX_2(LH_2)_2]$ (X = Cl, Br, I) and $[PtX_2(LH_2)_2]$ (X = Cl, I) were prepared and characterized by elemental analyses and spectroscopic (IR, far-IR, Raman) studies. All data are discussed in terms of the nature of bonding in conjunction with assigned structures. The LH_2 molecule behaves as a monodentate ligand binding through the sulfur atom. Monomeric square planar structures are assigned for the metal complexes in the solid state; the 1:2 complexes have the *trans* geometry. A detailed comparison of the new complexes with the corresponding monothiooxamide complexes is also presented.

Introduction

While the origin of crystal engineering has its roots in the understanding and control of inter-molecular interactions (weak and strong hydrogen bonds, halogen-halogen interactions, $\pi...\pi$ stacking interactions, van der Waals forces, *etc.*) in *organic* solids [1 - 3], in practice the field has grown to include materials that contain both inorganic and organic moieties [4 - 7]. Contributions to crystal engineering from organometallic and coordination chemistry are important because scientists are becoming more and more interested in creating functional materials [8 - 10], and a variety of magnetic, catalytic and electronic properties stems from the presence of transition metal ions [11].

Hydrogen bonding in organic crystals has been established as a reliable force for organic crystal engineering [2, 3, 12, 13], but it has only recently been introduced as a tool for the supramolecu-

lar assembly of coordination complexes by Mingos and coworkers [14, 15], and others [16 - 23]. These groups examined the efficacy of the hydrogen bond in the crystal engineering of transition-metal systems. By reacting metal ions with ligands that contain both efficient metal coordination sites and peripheral hydrogen bonding functionalities, assembly can be dictated by intermolecular hydrogen bonding interactions. Supramolecular synthons [24 - 26] may involve self-complementary (homomeric) hydrogen bonds, *e. g.* the well-known carboxylic acid dimer or the less-known neutral primary amide dimer, and heteromeric (but still complementary) hydrogen bond interactions, *e. g.* the carboxylic acid-primary amide interaction.

We have recently become interested in the crystal engineering of hydrogen bonded coordination complexes. Our emphasis is on coordination complexes with peripheral hydrogen bonding substituents, and our goal is to create novel supramolecular structures

based on hydrogen bonding interactions between simple metal complexes. This project can be regarded as an extension of our work in the area of coordination polymers [27 - 30]. We report herein the first results of our efforts. This paper describes the full structural and spectroscopic characterization of monothiomalonamide ($H_2NCSCH_2CONH_2$), hereafter abbreviated as LH_2, and its preliminary employment as ligand in palladium(II) and platinum(II) chemistry.

## Results and Discussion

Preliminary considerations

The development of the coordination chemistry of amides and thioamides is a central theme in transition metal chemistry. Research in this area ranges from solution of pure chemical [31, 32] and spectroscopic [33] problems to biological modeling applications [34] and advanced materials chemistry [35 - 37].

Over the last eight years, we have been reporting results of our efforts towards developing the chemistry, thermal properties and vibrational spectroscopy of d^8 and d^9 metal complexes with malonamide ($H_2NCOCH_2CONH_2$) [38 - 40] and dithiomalonamide ($H_2NCSCH_2CSNH_2$) [41, 42] as ligands. In contrast to the obtained large body of knowledge, complexes of monothiomalonamide ($H_2NCSCH_2CONH_2$, LH_2) have not been investigated, although this class of compounds could offer unique features in terms of structural, magnetic and spectroscopic properties. From the crystal engineering point of view, LH_2 contains four hydrogen bonding functionalities which can act as supramolecular synthons on simple coordination complexes.

The above considerations prompted us to begin a systematic study of the coordination chemistry of monothiomalonamide. Here we report on the preparation and characterization of the free ligand and its complexes with palladium(II) and platinum(II). Palladium(II) and platinum(II) were selected as metal sources because we expected that they would form coordinative bonds only to the sulfur atom, thus leaving both -NH_2 groups and the amide oxygen available for hydrogen bonding interactions. Special attention is given in the interpretation of the vibrational spectra of LH_2 and its complexes.

Synthesis and characterization of cis-LH_2 and trans-LH_2

Monothiomalonamide had been synthesized previously [43] by the reaction of cyanoacetamide and hydrogen sulfide in methanol at elevated temperatures according to eq. (1). We performed the reaction several times and were surprised to see that the

$$NCCH_2CONH_2 + H_2S \xrightarrow[110\,°C]{MeOH} H_2NCSCH_2CONH_2 \quad (1)$$
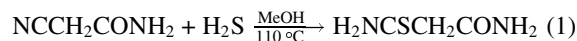
experiments were not reproducible. Sometimes a yellow powder could be isolated, whereas in other experiments the final product was a white powder. Both solids had identical melting points (110 °C) and their microanalyses (C, H, N, S) were consistent with the expected formula $H_2NCSCH_2CONH_2$; however, the two solids had different FT-IR and FT-Raman spectra. We suspected that two modifications of LH_2 existed and this turned out to be the case. A solution of the white powder in Me_2CO was layered with *n*-hexane. Slow mixing yielded a mixture of yellow and colourless crystals. X-ray crystallographic studies showed these materials to be *cis*-LH_2 and *trans*-LH_2, respectively (see below).

In the DTA curves of both modifications of LH_2 two major peaks appear: a very sharp peak at 110 °C that can be ascribed to the melting process, since no mass loss occurs in the TG curve, and a rather broad peak between 130 and 210 °C which is due to the evaporation or decomposition of the product. However, the thermogram of the *cis* form exhibits a weak additional signal at 83.5 °C (Fig. 1) which can be assigned to a phase transition. This transformation is irreversible, since after cooling to room temperature and again heating no transition occurs anymore. These experimental observations have been checked by IR and Raman spectroscopy. Indeed, a sample of
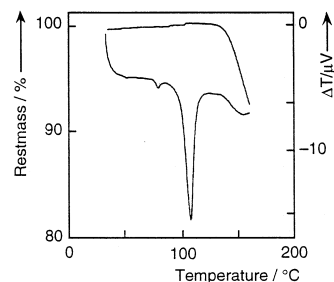

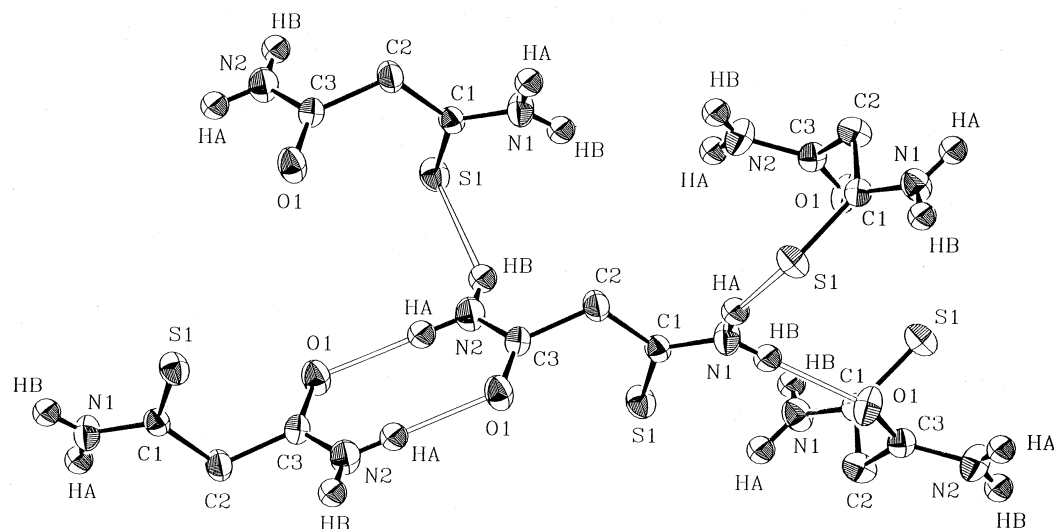Fig. 1. The TG and DTA curves of *cis*-LH_2.

Fig. 2. A part of the crystal structure of *cis*-LH$_2$ showing five molecules. Open bonds indicate H-bonds.

Table 1. Interatomic distances, angles and dimensions of the unique hydrogen bonds (distances in Å and angles in °) for *cis*-LH$_2$.

Interatomic distances		Angles	
S(1)-C(1)	1.678(1)	N(1)-C(1)-C(2)	114.5(1)
N(1)-C(1)	1.313(2)	N(1)-C(1)-S(1)	122.2(1)
N(2)-C(3)	1.326(2)	C(2)-C(1)-S(1)	123.3(1)
C(3)-O(1)	1.237(2)	C(1)-C(2)-C(3)	113.9(1)
C(1)-C(2)	1.514(2)	O(1)-C(3)-N(2)	121.8(1)
C(2)-C(3)	1.515(2)	O(1)-C(3)-C(2)	120.4(1)
		N(2)-C(3)-C(2)	117.8(1)

D^a-H···A^b	D^a···A^b	H···A^b	D^a-H···A^b
N(1)-HA(N1)···S(1)$^{\#1}$	3.452(1)	2.60(2)	161(1)
$[x, {}^1/_2 - y, -{}^1/_2 + z]$			
N(1)-HB(N1)···O(1)$^{\#2}$	2.860(1)	1.99(2)	164(2)
$[1 - x, -{}^1/_2 + y, {}^1/_2 - z]$			
N(2)-HA(N2)···O(1)$^{\#3}$	2.929(2)	2.05(2)	177(2)
$[-x, 1 - y, 1 - z]$			
N(2)-HB(N2)···S(1)$^{\#4}$	3.500(1)	2.78(2)	145(2)
$[-1 + x, y, z]$			

^{a} D = donor atom; ^{b} A = acceptor atom.

pure *cis*-LH$_2$ exhibits the typical vibrational pattern of the *trans* form after being heated up to 90 °C and cooled to room temperature.

Selected bond distances and angles for *cis*-LH$_2$ and *trans*-LH$_2$, and details of the H-bonds present in these compounds are given in Tables 1 and 2. Figs. 2 and 3 show perspective views of the two forms of LH$_2$ with the atomic numbering scheme.

The bond lengths and angles are very similar in both forms of LH$_2$ and can be compared to those of other molecules containing primary amide [44] or thioamide [45, 46] groups. The lengths of the C-O, C-S and C-N bonds indicate a resonance structure for both the -CONH$_2$ and -CSNH$_2$ groups in the molecule in which these bonds possess a high degree of double-bond character [44, 46]. The crystal structures of *cis* - and *trans*-LH$_2$ are stabilized by a network of intermolecular hydrogen bonds (see below); general views of the hydrogen bonding schemes are included in Figs. 2 and 3.

The *cis* form of LH$_2$, in which oxygen and sulfur atoms are in a *cis* position, can be characterized by a C_{2h} factor group symmetry deduced from the $P2_1/c$ space group [47]. The amide groups are mutually associated by hydrogen bonds to give cyclic $R_2^2(8)$ dimers [12, 35], generating a local inversion centre. The hydrogen atoms which are *anti*-planar to oxygen or sulfur atoms form catemeric amide-thioamide $C(6)$ interactions which, after combination of these chain motives, associate to $R_2^1(8)$ helices, creating a 3D network. The $R_4^2(8)$ motif, frequently seen in primary amide-containing molecules, is also present and generates an eight-membered ring system. When the intermolecular associations are considered per functional group, it can be seen that the thioamide -NH$_2$ group is associated with O- and S-atoms. The amide -NH$_2$ group takes part in cyclic amide-amide associations on one hand and catemeric N-H···S interactions on the other; the latter can, due to the large N···S distance and the small
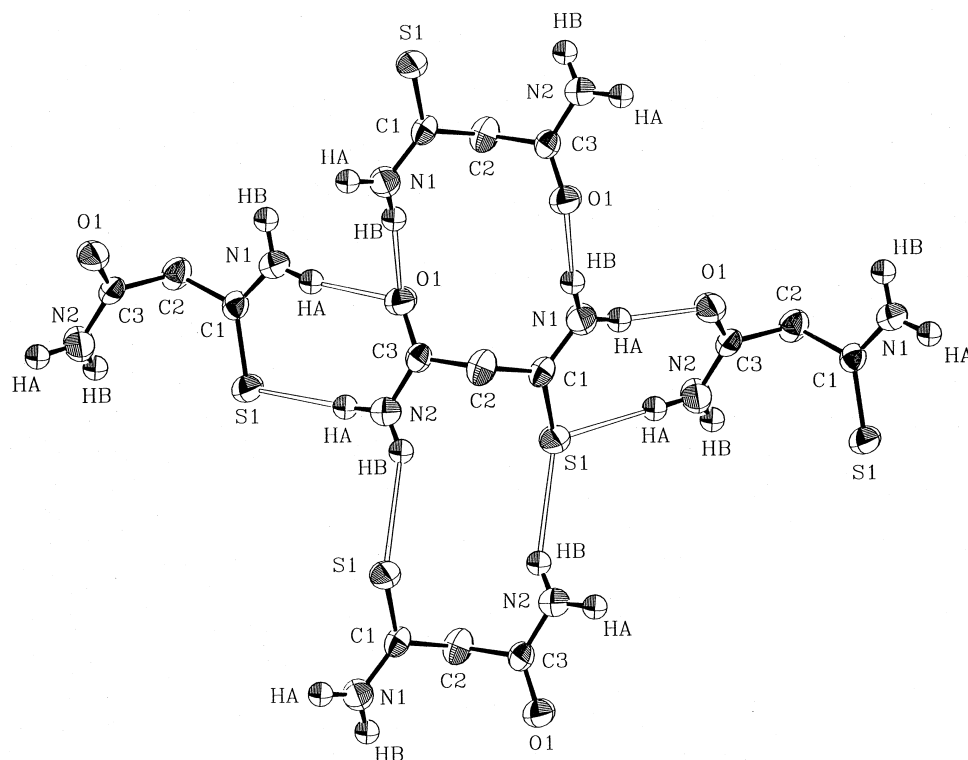
Fig. 3. A part of the crystal structure of *trans*-LH$_2$ showing five molecules. Open bonds indicate H-bonds.

Table 2. Interatomic distances, angles and dimensions of the unique hydrogen bonds (distances in Å and angles in °) for *trans*-LH$_2$.

Interatomic distances		Angles	
S(1)-C(1)	1.666(2)	N(1)-C(1)-C(2)	115.9(1)
N(1)-C(1)	1.312(2)	N(1)-C(1)-S(1)	123.5(1)
N(2)-C(3)	1.311(2)	C(2)-C(1)-S(1)	120.6(1)
C(3)-O(1)	1.234(2)	C(1)-C(2)-C(3)	110.8(1)
C(1)-C(2)	1.514(2)	O(1)-C(3)-N(2)	122.3(1)
C(2)-C(3)	1518(2)	O(1)-C(3)-C(2)	120.6(1)
		N(2)-C(3)-C(2)	117.1(1)

D^a-H···A^b	D^a···A^b	H···A^b	D^a-H···A^b
N(1)-HA(N1)···O(1) [$x, -y, {}^1/_2 + z$]	2.954(2)	2.09(2)	170(1)
N(1)-HB(N2)···O(1) [${}^1/_2 - x, {}^1/_2 + y, -z$]	2.866(2)	2.02(2)	171(2)
N(2)-HA(N2)···S(1) [$x, -y, -{}^1/_2 + z$]	3.485(2)	2.58(2)	176(2)
N(2)-HB(N2)···S(1) [$-x, 1 - y, -z$]	3.542(2)	2.76(2)	153(2)

^{a} D = donor atom; ^{b} A = acceptor atom.

N-H···S angle, hardly be described as efficient hydrogen bonds.

The factor group symmetry of the needle-like *trans* form is also C_{2h}, deduced from the $C\,2/c$ space group. Crystallographically equivalent molecules are stacked along the b -axis. The primary basis set is given by $N_1 = C(6)C(6)R_2^2(12)R_2^2(12)$. Both $C(6)$ chains give rise to cyclic amide-thioamide $R_2^2(8)$ dimers without local inversion symmetry since mixed associations are considered. The typical $R_4^2(8)$ profile is not present. This modification is exclusively characterized by amide-thioamide interactions, with the N(2)-HB(N2)···S(1) hydrogen bond being very weak (small N-H···S angle).

Fig. 4 illustrates the IR spectra of the *cis* and *trans* forms of LH$_2$ in the 4000 - 500 cm^{-1} region. The full solid-state vibrational analysis of *trans*-LH$_2$ is given in Table 3. Assignments have been given in comparison with the data obtained for monothiooxamide (H$_2$NCSCONH$_2$) [48], and have been assisted by NH$_2$/ND$_2$ and CH$_2$/CD$_2$ isotopic substitutions as well as low temperature IR spectroscopy.

Concerning the positions of the NCO fundamentals in the spectra of *cis*-LH$_2$ and *trans*-LH$_2$, it can be clearly seen that the ν(C=O) vibration of the former is situated at higher frequencies and its ν(CN$_O$) at lower frequencies, indicating a more polar character of the amide function in the latter. For example, the room temperature IR spectrum of *cis*-LH$_2$ exhibits the ν(C=O) and ν(CN$_O$) bands at 1672

Table 3. The full vibrational analysis[a] (cm^{-1}) of the *trans* form of monothiomalonamide.

H2NCSCH2CONH2				D2NCSCD2COND2		Assignments
IR[b]		Raman[b]		IR[b]	Raman[b]	
−196 °C	20 °C	20 °C	−196 °C	20 °C	20 °C	
3377 s	3388 m					$\nu_{asym}(N_OH_2)$
3282 s	3296 m					$\nu_{asym}(N_SH_2)$
3160 s	3165 s	3161 [2]				$\nu_{sym}(N_OH_2)$
3090 s	3101 m	3105 [2]				$\nu_{sym}(N_SH_2)$
2977 w	2978 w	2978 [3]				$\nu_{asym}(CH_2)$
2939 vw	2939 vw	2934 [4]				$\nu_{sym}(CH_2)$
			2556 s	2562 m	2562 [3]	$\nu_{asym}(N_OD_2)$
			2469 m	2482 m	2480 [5]	$\nu_{asym}(N_SD_2)$
			2340 m	2346 m	2355 [3]	$\nu_{sym}(N_OD_2)$
			2294 s	2309 s	2309 [4]	$\nu_{sym}(N_SD_2)$
					2217 [1]	$\nu_{asym}(CD_2)$
					2125 [3]	$\nu_{sym}(CD_2)$
1660 vs	1659 vs	1662 [2]	1648 vs	1651 vs		$\nu(C=O)$
			1637 vs	1639 vs	1605 [3]	$\nu(C=O)$
1604 s	1599 m	1591 [1]				$\delta(NH_2)$
1592 s						$\delta(NH_2)$
1455 s	1450 s	1457 [3]	1428 s	1474 s	1469 [4]	$\nu(CN_S)$
1437 m	1437 sh	1433 [2]				$\delta(CH_2)$
1416 m	1415 m	1415 [3]	1448 m	1442 m	1441 [4]	$\nu(CN_O)$
			1417 w	1415 w	1410 [2]	$\nu(CN_O)$
1312 m	1311 m	1299 [4]				$\omega(CH_2)$
			1220 m	1215 m	1214 [2]	$\delta(ND_2)$
			1192 m	1194 m	1200 [1]	$\delta(ND_2)$
1153 m	1152 m	1147 [1]				$\rho(N_SH_2)$
1111 vw	1110 sh					$\rho(N_OH_2)$
1103 w		1103 [3]				$\rho(N_OH_2)$
					1079 [1]	$\delta(CD_2)$
1018 s	1015 s	1011 [3]	1028 m	1030 m	1029 [1]	$\nu_{asym}(CCC)$
958 m	956 m					$\rho(CH_2)$
			935 m	942 mb	942 [2]	$\rho(ND_2)$
			880 w	879 w	882 [1]	$\omega(CD_2)$
			838 w		836 [1]	$\omega(CD_2)$
914 w	911 vw	908 [6]	810 m	809 m	806 [5]	$\nu_{sym}(CCC) + \nu(CS)$
822 m	810 sh					$\omega(N_SH_2)$
764 s						$\omega(N_OH_2)$
748 m	747 m	732 [2]				$\omega(N_OH_2)$
			715 m	713 w		$\rho(CD_2)$
			703 w	692 w	699 [1]	$\rho(CD_2)$
687 w						$\delta(NCO) + \delta(NCS)$
681 w	681 vw	684 [10]	649 m	648 m	647 [10]	$\delta(NCO) + \delta(NCS)$
			625 m			$\omega(N_SD_2)$
			620 m	610 m	616 [1]	$\omega(N_SD_2)$

and 1400 cm^{-1}, respectively, while the corresponding modes for *trans*-LH$_2$ are situated at 1659 and 1415 cm^{-1}. The significant shifts that these bands undergo upon deuteration are indicative of coupling effects with $\delta(NH_2)$.

From the frequencies of the $\nu(CN_S)$ fundamentals similar conclusions can be drawn for the thioamide group of the ligand forms. The lower IR frequency of $\nu(CN_S)$ in *cis*-LH$_2$ (1440 cm^{-1}) compared to that in *trans*-LH$_2$ (1450 cm^{-1}) indicates a less polar character of the thioamide group in the former, leading to a decreased double bond character for the C-N bond.

The stability of both modifications of LH$_2$ depends on a number of parameters. The *trans* form appears to be more efficiently stacked which may

Table 3 (continued).

	H$_2$NCSCH$_2$CONH$_2$				D$_2$NCSCD$_2$COND$_2$		Assignments
IR^b		Raman^b		IR^b	Raman^b		
−196 °C	20 °C	20 °C	−196 °C	20 °C	20 °C		
606 s	597 m	584 [1]					$T\alpha$(N$_S$H$_2$)
			594 m				ω(N$_O$D$_2$)
		584 w		584 w	560 [1]		ω(N$_O$D$_2$)
565 s	554 m	560 [1]					τ(N$_O$H$_2$)
			550 m	544 sh	546 [1]		τ(N$_S$D$_2$)
536 m	533 m	533 [3]		527 sh	517 [3]		δ(CCC)
			518 m	509 m			τ(N$_O$D$_2$)
		474 [5]					various
	447 m	439 [2]		427 m	426 [2]		NCO + NCS
	414 vs						defor-
	364 vs						mations
		337 [5]		339 vs	346 [3]		d
		218 [3]			218 [3]		d
		198 [3]			189 [3]		d
	150 sb	153 [4]			153 [3]		d
	120 m				122 [7]		d
					101 [15]		d

^{a} Overtones and combination bands have been omitted; ^{b} Fourier-transform spectra; ^{c} data in the 4000 - 500 cm^{-1} region; ^{d} various deformations and lattice vibrations; b: broad; m: medium; s: strong; sh: shoulder; v: very; w: weak. The subscript O denotes the amide group, while the subscript S refers to the thioamide function.

result in an increased overall stability, since this modification does not undergo any phase transition. The empirical rules for hydrogen bonding, formulated by Etter [49], provide additional confirmation for the stability trend. Concerning amides and thioamides, a N$_S$-H group is a better hydrogen donor than N$_O$-H, a fact that can be attributed to the increased contribution of the ionic resonance form to the structure in thioamides compared to that in amides [50]. Moreover, a CO group is a better hydrogen acceptor than a CS group because the oxygen atom is clearly harder according to the HSAB classification and more basic than sulfur. Thus, it is clear why the *trans* form is more stable than the *cis* form: all N$_S$-H groups are hydrogen-bonded to CO groups and this is not the case for the *cis* form.

This difference in stability is then confirmed by thermal analysis and recrystallization experiments. Concerning the first technique, only the *cis* form undergoes a phase transition (Fig. 1) which appears to be irreversible. As far as the recrystallization behaviour is concerned, when the *cis* or the *trans* form is separately dissolved in a variety of organic solvents, including alcohols, only the colourless needles of the *trans* conformation are normally isolated. The simultaneous occurrence of both crystal forms
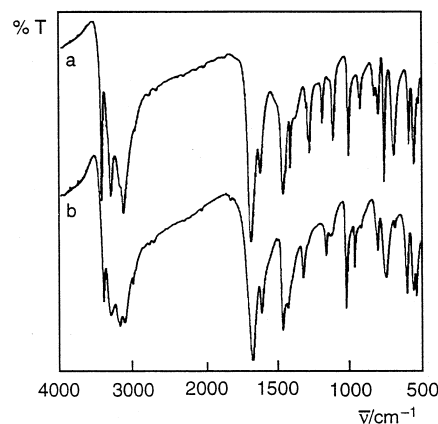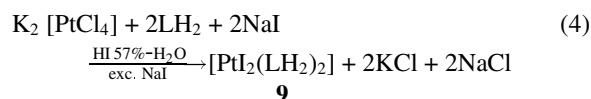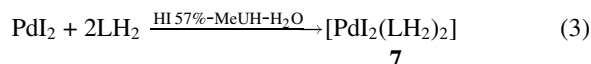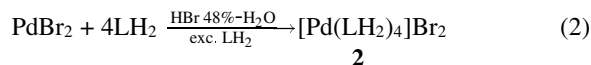

Fig. 4. The FT-IR spectra of *cis*-LH$_2$ (a) and *trans*-LH$_2$ (b).

in some experiments may be due to kinetic phenomena [51]. Why monothiomalonamide does exist in a *cis* conformation that does not transform spontaneously to the *trans* form may be explained by the presence of cyclic amide-amide associations which partially compensate for other destabilizing factors; these associations can be broken only when external energy is applied to the crystal or solvent molecules break up the structure.

Preparation and physical properties of the complexes

The Experimental Part lists nine new complexes. The elemental analyses of the isolated compounds agree with the assigned formulae. The complexes have the formulae $[Pd(LH_2)_4]X_2$ (X = Cl, **1**; X = Br, **2**), $[Pt(LH_2)_4]X_2$ (X = Br, **3**; X = I, **4**), $[PdX_2(LH_2)_2]$ (X = Cl, **5**; X = Br, **6**; X = I, **7**) and $[PtX_2(LH_2)_2]$ (X = Cl, **8**; X = I, **9**). The preparation of three representative complexes is summarized in eqs (2) - (4):

$$PdBr_2 + 4LH_2 \xrightarrow[\text{exc. } LH_2]{\text{HBr 48\%-}H_2O} [Pd(LH_2)_4]Br_2 \qquad (2)$$
$$\mathbf{2}$$

$$PdI_2 + 2LH_2 \xrightarrow{\text{HI 57\%-MeUH-}H_2O} [PdI_2(LH_2)_2] \qquad (3)$$
$$\mathbf{7}$$

$$K_2[PtCl_4] + 2LH_2 + 2NaI \qquad (4)$$
$$\xrightarrow[\text{exc. NaI}]{\text{HI 57\%-}H_2O} [PtI_2(LH_2)_2] + 2KCl + 2NaCl$$
$$\mathbf{9}$$

A few synthetic points deserve comment. First, the formation of palladium(II) and platinum(II) complexes with neutral monothiomalonamide is feasible only in acidic solvent mixtures ($HX-H_2O$ or HX-MeOH), which prevent formation of complexes with the monoanionic form of the ligand. Second, three of the reactions studied are molar-ratio dependent. For example, employing a molar ratio 1 : 2 for $PdCl_2 : LH_2$ the neutral complex $[PdCl_2(LH_2)_2]$ was obtained; when an excess of LH_2 was present (molar ratio $Pd^{II} : LH_2 = 1 : 5$) the ionic 1 : 4 complex was isolated. Third, the 1:2 complexes have a *trans* geometry (see below) and can be prepared directly from the $[MX_4]^{2-}$ ions ($MX_2 + 2X^-$; M = Pd, Pt) by reaction with the ligand. The isolation of *trans* (and not *cis*) complexes can be explained by the fact that LH_2 has a greater *trans effect* [52] compared to X^-. Ideal routes for the preparation of *cis*-$[MX_2(LH_2)_2]$ would be the reactions of $[M(LH_2)_4]X_2$ with an excess of X^-; unfortunately the attempted reactions failed to give pure products. A final point of interest is the fact that all complexes could be prepared starting either from the *cis* or the *trans* form of LH_2.

The prepared complexes are microcrystalline or powder-like, stable in the normal laboratory atmosphere and soluble only in DMF and DMSO. The 1:4 complexes have a moderate solubility in H_2O. We had hoped to structurally characterize some complexes by single-crystal X-ray crystallography, but were thwarted on numerous occasions

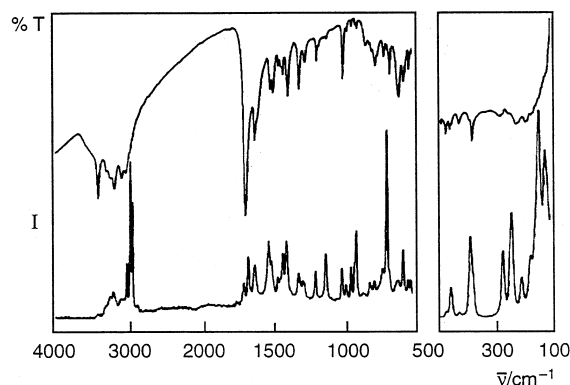Fig. 5. The FT-IR and FT-Raman spectra of $[Pd(LH_2)_4]Cl_2$ (**1**).

by very small crystal dimensions or twinning problems. Thus, the characterization of the complexes remains to be based on spectroscopic techniques.

Vibrational spectra of the complexes

Tables 4 and 5 give diagnostic IR and far-IR bands for the 1:4 and 1:2 complexes, respectively. The IR, far-IR and Raman spectra of **1** are shown in Fig. 5. Fig. 6 illustrates the IR spectrum of **5**.

Assignments in Tables 4 and 5 have been given in comparison with the data obtained for the two forms of LH_2, for complexes *trans*-$[PdX_2(MTOH_2)_2]$ and $[Pd(MTOH_2)_4]Cl_2$ (X = Cl, Br, I; $MTOH_2 = H_2NCSCONH_2$) [53], for complexes containing primary amide [39, 40, 43, 54, 55] or thioamide [42, 56 - 58] groups, and have been assisted by H/D isotopic substitutions. Low-frequency assignments were also assisted by studying the variation in band position with changing metal ion (for a given X) and X (for a given metal) and the literature [42, 53, 58 - 62]. As a general remark, we must emphasize that some modes are strongly coupled and, thus, the proposed assignments should be regarded as approximate descriptions of the vibrations. Since all diagnostic vibrational frequencies and their assignments have been tabulated, the spectroscopic discussion will be confined only to the most important features in relation to the coordination mode of LH_2, and to the structures of its palladium(II) and platinum(II) complexes.

Considering the amide function of the complexes, the spectra show the typical bands of neutral primary amide groups [63]. The absence of large systematic

Table 4. Most characteristic and diagnostic IR fundamentals (cm^{-1}) of the cationic complexes $[Pd(LH_2)_4]X_2$ (X = Cl, **1**; X = Br, **2**) and $[Pt(LH_2)_4]X_2$ (X = Br, **3**; X = I, **4**).

1	2	3	4	Assignments
3403 s	3398 m	3394 s	3396 m	$\nu_{asym}(N_OH_2)$
3282 sh	3282 m	3277 m	3272 m	$\nu_{asym}(N_SH_2)$
3226 m	3235 m	3235 s		$\nu_{asym}(N_SH_2)$
3177 m	3179 m	3177 s	3170 m	$\nu_{sym}(N_OH_2)$
3076 w	3079 m	3082 s	3090 m	$\nu_{sym}(N_SH_2)$
1674 vs	1670 vs	1670 vs	1673 vs	$\nu(C=O)$
1609 m	1605 m	1605 m	1627 m	$\delta(N_SH_2)$
1598 sh	1600 m	1598 w	1595 m	$\delta(N_OH_2)$
1501 m	1501 m	1503 m	1506 w	$\nu(CN_S)$
1481 m	1481 m	1481 m	1481 s	$\nu(CN_S)$
1376 m	1369 m	1369 m	1387 m	$\nu(CN_O)$
1175 m	1172 w	1171 m	1168 m	$\rho(N_SH_2)$
1105 vw	1106 w	1107 w	1118 vw	$\rho(N_OH_2)$
832 wb	799 wb	800 m	777 w	$\omega(N_SH_2)$
763 m	738 sh	739 sh	714 m	$\omega(N_OH_2)$
703 w	698 m	698 m	692 m	$\nu(CS)$
596 m	588 m	603 m	607 m	$\tau(N_SH_2)$
566 m	564 w	564 m	538 w	$\tau(N_OH_2)$
285 wb	282 w	280 w	279 w	$\nu(MS)$
249 w	262 w	253 w		$\nu(MS)$

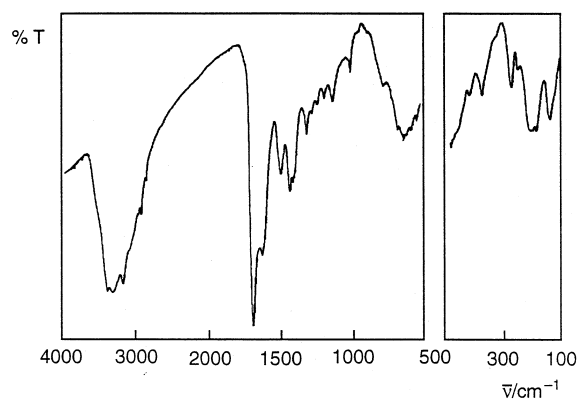The subscript O denotes the amide group, while the subscript S refers to the thioamide function; M = Pd, Pt.

Fig. 6. The FT-IR spectrum of $[PdCl_2(LH_2)_2]$ (**5**).

shifts of the characteristic amide modes in the vibrational spectra of the complexes, compared with the frequencies of the corresponding modes in the spectra of both forms of LH_2, implies that there is no interaction between the amide group and the metal ions.

Considering the thioamide function of the complexes, their vibrational spectra exhibit the typical bands of the primary thioamide groups [48]. The $\nu(CN_S)$ mode is situated at higher frequencies in
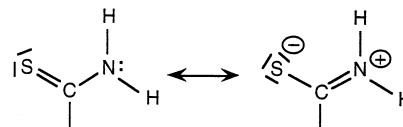

Fig. 7. The two canonical forms of the primary thioamide function.

the spectra of the complexes than for *cis-* or *trans-*LH_2; this shift is consistent with thioamide-sulfur coordination [42, 53, 58]. Although the $\nu(CS)$ vibration is not pure [48], the bands with high $\nu(CS)$ character in the spectra of the 1:4 complexes seem to be situated at lower frequencies than for free ligand forms, also indicating sulfur coordination [42, 53, 58]. On coordination *via* sulfur, the positively charged metal ions stabilize the negative charge on the sulfur atom. The thioamide function now occurs in its polar resonance form (Fig. 7) and, thus, the double bond character of the CN bond increases, while the double bond character of the CS bond decreases. The $\nu(CS)$ band(s) could not be assigned in the spectra of the 1 : 2 complexes.

The more polar character of the thioamide function explains the lower values of $\nu_{asym}(N_SH_2)$ and $\nu_{sym}(N_SH_2)$, compared with the $\nu_{asym}(N_OH_2)$ and $\nu_{sym}(N_OH_2)$ modes [50]. The bands due to the deformation, rocking, wagging and twisting-NH_2 vibrations are clearly split, with the higher frequency modes being assigned to thioamide vibrations.

The far-IR spectrum of **4** shows a band of weak intensity at 279 cm^{-1}, assigned to the Pt-S E_u stretching vibration of the square planar complex cation (point group: D_{4h}) [64]. Two $\nu(MS)$ bands are observed in the spectra of the other 1:4 complexes; this splitting may be due to a distortion of the ideal square planar structure or to a crystal packing effect [59, 60]. The two expected Raman-active $\nu(MS)$ vibrations (A_{1g}, B_{1g} under D_{4h} symmetry) are observed in the spectra of all four complexes. Despite the fact that Pt is heavier than Pd, the frequency of the $\nu(PtS)$ vibration is almost the same as that of $\nu(PdS)$ indicating an increased contribution of back-donation in the platinum(II) complexes.

The presence of one terminal $\nu(MX)$ (M = Pd, Pt; X = Cl, Br, I) vibration (B_{3u} under D_{2h} symmetry) and one $\nu(MS)$ vibration (B_{2u} under D_{2h} symmetry) in the low-frequency IR spectra of the 1:2 complexes **5 - 9** confirms their *trans* square planar geometry [59 - 61].

[PdX₂(LH₂)₂]			[PtX₂(LH₂)₂]		Assignments
X = (**5**)	X = Br (**6**)	X = I (**7**)	X = Cl (**8**)	X = I (**9**)	
3399 s	3399 m	3415 m	3451 m	3412 m	$\nu_{asym}(N_OH_2)$
3327 s	3293 s	3309 m	3324 m	3307 m	$\nu_{sym}(N_OH_2)$
		3262 m			$\nu_{sym}(N_OH_2)$
3181 s	3177 m	3187 w	3178 w	3185 w	$\nu(N_SH_2)$
3079 sh	3090 sh	3014 wb	3052 mb	3014 wb	$\nu(N_SH_2)$
1672 vs	1669 vs	1665 vs	1669 vs	1666 vs	$\nu(C=O) + \delta(N_SH_2)$
1610 m	1606 m	1602 m	1600 s	1602 m	$\delta(N_OH_2)$
1476 m	1476 m	1489 m	1498 m	1491 s	$\nu(CN_S)$
1395 m	1384 w	1418 m	1380 m	1418 s	$\nu(CN_O)$
1175 w	1172 vw	1183 m	1179 vw	1183 m	$\rho(N_SH_2)$
1117 w	1113 vw	1096 w	1098 w	1096 m	$\rho(N_OH_2)$
			333 s		$\nu(PtCl)$
317 m					$\nu(PdCl)$
278 m	276 m	281 w	278 w	282 w	$\nu(MS)$
	255 m				$\nu(PdBr)$
		216 sb		203 m	$\nu(MI)$

Table 5. Most characteristic and diagnostic IR fundamentals (cm^{-1}) of the 1 : 2 palladium(II) and platinum(II) complexes.

The subscript O denotes the amide group, while the subscript S refers to the thioamide function; M = Pd, Pt.

The frequency of the ν(PdS) vibration is lowered on going from **1** to **5** and also from **2** to **6**, implying a stronger Pd-S bond in complexes in which the Pd^{II} atom is bonded to four sulfur atoms; this difference in Pd-S bond strength is reflected in the frequencies of ν(CN$_S$), which follow the sequences **5** < **1** and **6** < **2**.

Structural proposals and spectroscopic trends

From the above results, it is concluded that in all the complexes the thioamide sulfur atom is the donor atom to palladium(II) and platinum(II). The proposed mononuclear, square planar structures for the 1:4 and 1:2 complexes are shown in Figs 8 and 9, respectively. The structures are certainly stabilized by intermolecular hydrogen bonds, as suggested by the position and profile of the -NH₂ bands in the vibrational spectra. In the absence of X-ray structural data, the conformation (*cis* or *trans*) of the coordinated ligand can not be deduced. Some clearcut spectral differences within a given series (1:4, 1:2) of complexes can be ascribed to different conformations of coordinated LH₂, which has a rather large freedom of movement as a monodentate ligand. For example, the overall vibrational profile of [Pt(LH₂)₄]I₂ differs from that of the other cationic complexes.

As it has been stated above, the Pd-S bond strength increases on going from the 1:2 to the 1:4 Pd^{II}/LH₂/X$^-$ (X = Cl, Br) complexes. This trend is due to a symbiotic effect [64], according to which soft ligands flock together in a complex with a soft
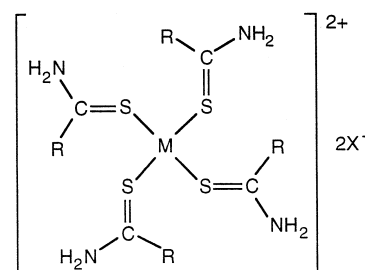

Fig. 8. D_{4h} symmetry for the square planar [M(LH₂)₄]$^{2+}$ cations (M = Pd, Pt; R = CH₂CONH₂; X = Cl, Br, I) present in complexes **1** - **4**.
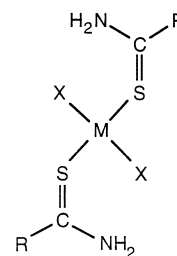

Fig. 9. The proposed *trans* square planar structure of the 1 : 2 complexes **5** - **9** (M = Pd, Pt; R = CH₂CONH₂; X = Cl, Br, I).

metal ion, like palladium(II). The tendency towards symbiosis of four soft ligands (LH₂) makes the mixed complexes of definitely soft and hard (or relatively soft) ligands, *i. e.*, complexes [PdCl₂(LH₂)₂] and [PdBr₂(LH₂)₂], less stable.

The ν(MS) frequencies in the present complexes are lower than in the complexes [M(AH₂)₂]Cl₂ (M =

Pd, Pt; AH$_2$ = dithiomalonamide) [42]; this is attributed to the absence of extra stabilization-due to the chelate effect- in the complexes of LH$_2$.

Comparison between the palladium(II) complexes of monothiomalonamide and monothiooxamide

The comparison between the coordinating abilities of monothiomalonamide (LH$_2$) and monothiooxamide (H$_2$NCSCONH$_2$, MTOH$_2$) [53] towards palladium(II) halides shows similarities and differences. Both molecules behave as monodentate ligands with the ligated atom being the neutral thioamide sulfur and form 1 : 2 complexes with a *trans* geometry. The bromide salt of [Pd(MTOH$_2$)$_4$]$^{2+}$ could not be synthesized, whereas compound [Pd(LH$_2$)$_4$]Br$_2$ forms rather easily, a fact that can be attributed to strong hydrogen bonding in the latter; the stronger hydrogen bonds between LH$_2$ and bromide ions favour the formation of an ionic compound when an excess of ligand is present. The ν(PdS) bands are found at much lower frequencies in the IR and Raman spectra of the LH$_2$ complexes compared to their MTOH$_2$ analogues, implying weaker Pd-S bonds in the former; for example, the ν(PdS) modes are situated at 285 and 249 cm^{-1} in the far-IR spectrum of [Pd(LH$_2$)$_4$]Cl$_2$, and at 340 and 321 cm^{-1} in the spectrum of [Pd(MTOH$_2$)$_4$]Cl$_2$ [53]. Electronic factors, such as a difference in the withdrawing properties between -CONH$_2$ and -CH$_2$CONH$_2$, may be responsible for this variation.

Concluding Comments and Perspectives

The *cis* and *trans* forms of free monothiomalonamide have been fully characterized by single-crystal X-ray crystallography and vibrational spectroscopy. However, the utility of these forms as supramolecular synthons in inorganic crystal engineering can presently not be evaluated, because crystal structures of metal complexes of LH$_2$ are not available. We strongly believe that the hydrogen bonding functionalities yield a variety of 1D, 2D or/and 3D architectures either through neutral (**5** - **9**) or ionic (**1** - **4**) intermediaries; in the latter case, the infinite assemblies created by ligand-counter ion hydrogen bonds are not, strictly speaking, ligand-based hydrogen bonded assemblies [12]. We continue our efforts to crystallize neutral metal complexes of LH$_2$ and substituted monothiomalonamides.

Experimental Section

All manipulations were performed under aerobic conditions using materials and solvents (Merck) as received; Water was distilled in-house. Crude LH$_2$ was synthesized as described earlier [43] by the reaction of methanolic solutions of NCCH$_2$CONH$_2$ and H$_2$S at elevated temperatures in a high-pressure vessel; the reaction took place at 110 °C for 1.5 h. We were able to isolate and structurally characterize both the *cis* and *trans* forms of the free ligand (see above). Elemental analyses (C, H, N, S) were conducted by the University of Ioannina, Greece, Microanalytical Service. IR spectra (4000 - 500 cm^{-1}) were recorded and averaged on a Bruker IFS 113v Fourier-transform (FT) spectrometer, using a liquid nitrogen-cooled MCT detector, with samples prepared as KBr pellets. FT far-IR spectra (500 - 50 cm^{-1}) were recorded on a Bruker IFS 113v spectrometer with a DTGS detector using polyethylene pellets. FT Raman data have been collected on a Bruker IFS 66v interferometer equipped with a FRA 106 Raman module and a Nd-YAG laser. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) experiments were performed on the SDT-2960 module from TA-instruments in a dinitrogen gas flow; sample weights of 5 - 15 mg and heating rates of 1 and 5 °C min^{-1} were used.

Preparation of the 1:4 complexes **1** - **4**

The 1:4 ionic complexes [Pd(LH$_2$)$_4$]X$_2$ (X = Cl, Br) and [Pt(LH$_2$)$_4$]X$_2$ (X = Br, I) were all prepared similarly. A total amount of 0.2 mmol of MX$_2$ was dissolved in 1.5 - 2.0 ml of the corresponding concentrated HX acid; hydrochloric (37%), hydrobromic (48%) and hydroiodic (57%) acids were used. The solution was diluted with H$_2$O (1 - 2 ml) and slowly added to a stirred solution of LH$_2$ (1.0 mmol) in H$_2$O (5 - 6 ml) and HX (0.2 ml). Upon addition of the metal salts, precipitates were obtained. Stirring was continued for 15 min. The precipitates were collected by filtration, washed with cold H$_2$O (2 $\times$ 3 ml), EtOH (3 $\times$ 5 ml) and copious amounts of Et$_2$O, and dried *in vacuo* over P$_4$O$_{10}$. Colours, yields and analytical results for the complexes are given below.

*[Pd(LH$_2$)$_4$]Cl$_2$ (***1***):* Pale yellow. Yield: 59%. – C$_{12}$H$_{24}$N$_8$O$_4$S$_4$Cl$_2$Pd (649.98): calcd. C 22.17, H 3.73, N 17.24, S 19.73; found C 22.50, H 3.82, N 17.39, S 20.26.

*[Pd(LH$_2$)$_4$]Br$_2$ (***2***):* Yellow. Yield: 42%. – C$_{12}$H$_{24}$N$_8$O$_4$S$_4$Br$_2$Pd (738.88): calcd. C 19.50, H 3.28, N 15.17, S 17.36; found C 19.88, H 3.37, N 15.32, S 17.66.

*[Pt(LH$_2$)$_4$]Br$_2$ (***3***):* Beige. Yield: 57%. – C$_{12}$H$_{24}$N$_8$O$_4$S$_4$Br$_2$Pt (827.56): calcd. C 17.41, H 2.93, N 13.54, S 15.50; found C 17.46, H 2.88, N 13.40, S 13.59.

*[Pt(LH$_2$)$_4$]I$_2$ (***4***):* Yellowish brown. Yield: 63%. – C$_{12}$H$_{24}$N$_8$O$_4$S$_4$I$_2$Pt (921.56): calcd. C 15.64, H 2.63, N 12.16, S 13.91; found C 15.34, H 2.44, N 12.30, S 14.00.

Compound	*cis*-LH$_2$	*trans*-LH$_2$
Chemical formula	C$_3$H$_6$N$_2$SO	C$_3$H$_6$N$_2$SO
Formula weight	118.16	118.16
Colour, habit	yellow prisms	colourless needles
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	5.602(3)	20.336(7)
b (Å)	9.055(2)	4.317(1)
c (Å)	10.945(5)	12.432(5)
β (°)	101.29(2)	92.16(1)
V (Å^3)	544.5(5)	1090.7(6)
Z	4	8
D_{calc} (g cm^{-3})	1.441	1.439
μ (mm^{-1})	0.472	0.471
$F(000)$	248	496
Radiation (Å)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)
Temperature (K)	298	298
Scan mode/speed (° min^{-1})	θ-2θ/3.5	θ-2θ/3.5
θ Range (°)	2.9 - 27.0	2.0 - 26.0
h, k, l Ranges	$-7 \rightarrow 0, 0 \rightarrow 11, -13 \rightarrow 13$	$-24 \rightarrow 24, 0 \rightarrow 5, 0 \rightarrow 15$
Measured reflections	1291	1118
Unique reflections	1174	1063
Reflections used [$I > 2 \sigma(I)$]	1111	974
Parameters refined	89	88
$[\Delta/\sigma]_{max}$	0.003	0.001
w^a	a = 0.0357; b = 0.1260	a = 0.0215; b = 0.6041
GoF (on F^2)	1.100	1.091
$R1^b$ [$I > 2\sigma(I)$]	0.0301	0.0286
$wR2^c$ [$I > 2\sigma(I)$]	0.0830	0.0786
$R1$ (all data)	0.0315	0.0315
$wR2$ (all data)	0.0845	0.0852
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e Å^{-3})	0.311/–0.206	–0.192/–0.211

Table 6. Summary of crystal data, data collection and structure refinement for X-ray diffraction study of the *cis* and *trans* forms of LH$_2$.

^{a} w = $1/[\sigma^2(F_o^2) + (\alpha P)^2 + bP]$ and P = $(\max(F_o^2,0) + 2F_c^2)/3$; ^{b} $R1 = \Sigma (|F_o| - |F_c| / \Sigma (|F_o|))$; ^{c} $wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$.

Preparation of the 1 : 2 complexes 5 - 9

The 1 : 2 neutral complexes [PdX$_2$(LH$_2$)$_2$] (X = Cl, Br, I) and [PtX$_2$(LH$_2$)$_2$] (X = Cl, I) were prepared in a rather similar manner, as follows: To a solution containing 0.4 mmol of the palladium(II) (Na$_2$[PdCl$_4$] · 3 H$_2$O, PdBr$_2$, PdI$_2$) or platinum(II) (K$_2$[PtCl$_4$]) starting material in concentrated HX (1 ml) and H$_2$O-MeOH (50:50 v/v, 4 ml) or in concentrated HX (2 ml) and aqueous NaX (20 mmol, 4 ml), respectively, was added dropwise a solution of LH$_2$ (0.8 mmol) in H$_2$O (7 ml). The reactions proceeded smoothly and precipitates formed within 5 min. The reaction mixtures were stirred at room temperature for 30 min after the first precipitate appeared. The solids were collected by filtration, washed with MeOH (2 × 5 ml) and Et$_2$O (3 × 10 ml), and dried *in vacuo* over silica gel. Colours, yields and analytical results for **5** - **9** are given below.

[PdCl$_2$(LH$_2$)$_2$] (5): Brown. Yield: 53%. – C$_6$H$_{12}$N$_4$O$_2$S$_2$Cl$_2$Pd (413.64): calcd. C 17.42, H 2.93, N 13.55, S 15.50; found C 17.33, H 2.80, N 12.99, S 16.01.

[PdBr$_2$(LH$_2$)$_2$] (6) Brown. Yield: 31%. – C$_6$H$_{12}$N$_4$O$_2$S$_2$Br$_2$Pd (502.54): calcd. C 14.34, H 2.41, N 11.15, S 12.76; found C 14.30, H 2.29, N 11.01, S 12.48.

[PdI$_2$(LH$_2$)$_2$] (7): Reddish brown. Yield: 72%. – C$_6$H$_{12}$N$_4$O$_2$S$_2$I$_2$Pd (596.54): calcd. C 12.08, H 2.03, N 9.39, S 10.75; found C 12.50, H 2.09, N 9.51, S 10.62.

[PtCl$_2$(LH$_2$)$_2$] (8): Salmon pink. Yield: 86%. – C$_6$H$_{12}$N$_4$O$_2$S$_2$Cl$_2$Pt (502.32): calcd. C 14.34, H 2.41, N 11.16, S 12.76; found C 14.76, H 2.50, N 11.36, S 13.41.

[PtI$_2$(LH$_2$)$_2$] (9): Chocolate brown. Yield: 61%. – C$_6$H$_{12}$N$_4$O$_2$S$_2$I$_2$Pt (685.22): calcd. C 10.52, H 1.77, N 8.18, S 9.36; found C 10.71, H 1.71, N 7.93, S 10.00.

Preparation of the deuterated complexes

The deuterated analogues of **1** - **9** were prepared on smaller synthetic scales as described for the normal complexes using LD$_2$ (prepared by recrystallization of LH$_2$ from D$_2$O twice) and deuterated solvents (D$_2$O, EtOD, MeOD, DCl, DBr, DI); the precipitates were not washed with Et$_2$O.

Unsuccessful synthetic attempts

Attempts to prepare complexes [Pd(LH$_2$)$_4$]I$_2$, [Pt(LH$_2$)$_4$]Cl$_2$ and [PtBr$_2$(LH$_2$)$_2$], using several prepar-

ative conditions (many ligand to metal molar ratios, various reaction times, a wide variety of solvent mixtures) failed. In the case of platinum(II), products of uncertain nature, with poor analytical results, were obtained. All efforts to prepare $[Pd(LH_2)_4]I_2$ led to the isolation of $[PdI_2(LH_2)_2]$ (**7**).

Crystal structure determinations

To obtain crystals suitable for single-crystal X-ray crystallography, a quantity of the powder of *trans*-LH$_2$ was dissolved in Me$_2$CO. Layering of *n*-hexane onto this solution gave a mixture of yellow prisms and colourless needles. The two materials were readily separable manually; the yellow and colourless crystals proved by single-crystal X-ray crystallography to be the *cis* and *trans* forms of LH$_2$, respectively. A crystal of *cis*-LH$_2$ with approximate dimensions $0.20 \times 0.40 \times 0.70$ mm and a crystal of *trans*-LH$_2$ with approximate dimensions $0.20 \times 0.50 \times 0.70$ mm were mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer. Crystal data and full details of the data collection and data processing are listed in Table 6. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range $11° < 2\,\theta < 23°$. Three standard reflections, monitored every 97 reflections, showed less than 3% intensity fluctuation and no decay. Lorentz, polarization and Ψ scan absorption corrections were applied using Crystal Logic software.

The structures were solved by direct methods using SHELXS-86 [65] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93 [66]. For both structures, all non-H atoms were readily located and refined with anisotropic thermal parameters. All H atoms were located by difference maps and their positions refined isotropically. Two X-ray crystallographic files for compounds *cis*-LH$_2$ and *trans*-LH$_2$, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge C82 1EZ, UK, under the numbers 103378 (*cis*-LH$_2$) and 103379 (*trans*-LH$_2$). Copies may be requested free of charge from the Director of CCDC (E-mail: deposit@ccdc.cam.ac.uk).

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