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Synthesis and structure of dilead(II) and dimanganese(II) complexes of macrocycles derived from 3,6-diformylpyridazine

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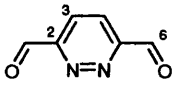
An improved synthesis of 3,6-diformylpyridazine **I** has been elaborated. The macrocyclic complexes $Pb_2L^1(ClO_4)_4$ **1** and $[Pb_2L^2][ClO_4]_4$ **2** were prepared from this precursor, 1,3-diaminopropane and lead(II) perchlorate in 1:1:1 and 2:2:1 ratios respectively. The ability of lead(II) perchlorate to template the formation of the two macrocycle ring sizes, L^1 = (2 + 2) and L^2 = (4 + 4), simply by alteration of the reagent ratio is unprecedented. Transmetallation of **1** or **2** with manganese(II) perchlorate and an excess of sodium thiocyanate led to the formation of $[Mn_2L^1(NCS)_4]$ **3**. Single-crystal X-ray analyses of **2** and **3** revealed that on transmetallation a ring contraction, (4 + 4) to (2 + 2), occurs. The two manganese(II) ions have irregular geometries and are inequivalent; one is six- whilst the other is seven-co-ordinate. Unusual single-atom > NCS bridging of the manganese ions occurs.

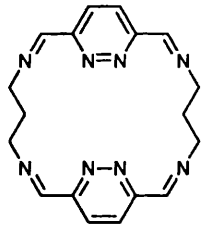
To our knowledge, acyclic oximes of general type L^3 (ref. 1) are the only examples to be derived from 3,6-diformylpyridazine, yet a large number of complexes of closely related acyclic ligands of general types L^4–L^6 have been studied.‡[2–4] Compounds L^4–L^6 are prepared from commercially available 3,6-dichloropyridazine.[2,3] In contrast to the large number of acyclic complexes prepared there has been only limited success in incorporating pyridazine into macrocycles, with the few known examples derived from 3,6-dichloropyridazine (*e.g.* L^7–L^9).[5]‡ To date, the pyridazine moiety in these macrocycles has failed to bridge the bound metal ions, and in some cases does not co-ordinate to the incorporated metal ion(s) at all.[5]§

Interest in these transition-metal complexes is due, in part, to their potential relevance as structural models for metalloproteins[7] and, in particular, to the ability of pyridazine to mediate magnetic exchange,[1–5] a property reminiscent of analogous phenol-bridged complexes.[8] Other physical and chemical properties, for example electrochemical behaviour, of the pyridazine-bridged complexes contrast with those of the phenolic complexes due to the different metal–metal separations and the softer donors.[1–5,8,9]

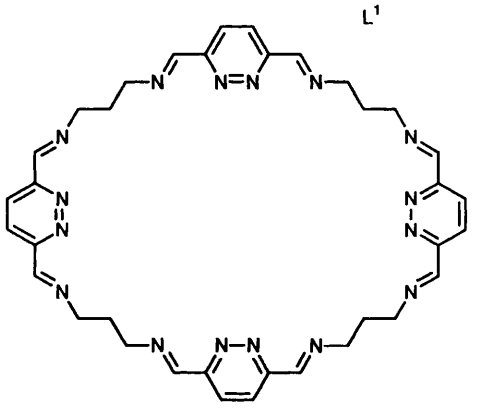
As part of our programme to introduce new 'head units' into Schiff-base macrocyclic chemistry[9,10] we decided to prepare 3,6-diformylpyridazine **I** and incorporate it into a macrocycle



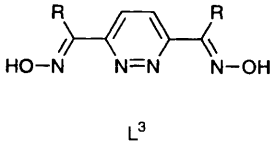
I



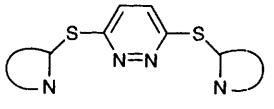
L^1



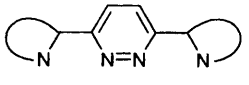
L^2



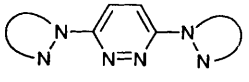
L^3



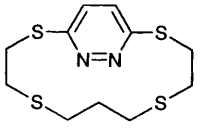
L^4



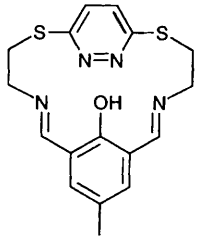
L^5



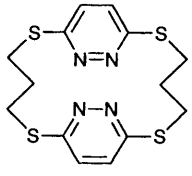
L^6



L^7



L^9



L^8

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‡ Analogous phthalazine derivatives are also known.

§ A phthalazine-containing macrocycle has been derived from 1,4-dihydrazinophthalazine (Aldrich) and is proposed to contain phthalazine-bridged metal ions.[6]

as the properties of the resulting complexes were expected to be of considerable interest. The use of this particular macrocycle precursor was expected to remedy the reported difficulties[5] in obtaining *pyridazine-bridged macrocyclic* complexes. We have recently communicated the successful preparation and structure determination of the first macrocycle to be derived from **I**, $[Pb_2L^2][ClO_4]_4$.[9] This lead complex is central to the synthesis of a wide range of transition-metal complexes by transmetallation reactions.[9] Herein we detail the synthesis and properties of the organic precursor **I**, the lead(II) complexes $Pb_2L^1(ClO_4)_4$ **1** and $[Pb_2L^2][ClO_4]_4$ **2**, and the manganese(II) complex $[Mn_2L^1(NCS)_4]$ **3**, prepared by transmetallation.

Results and Discussion

Synthesis of 3,6-diformylpyridazine I

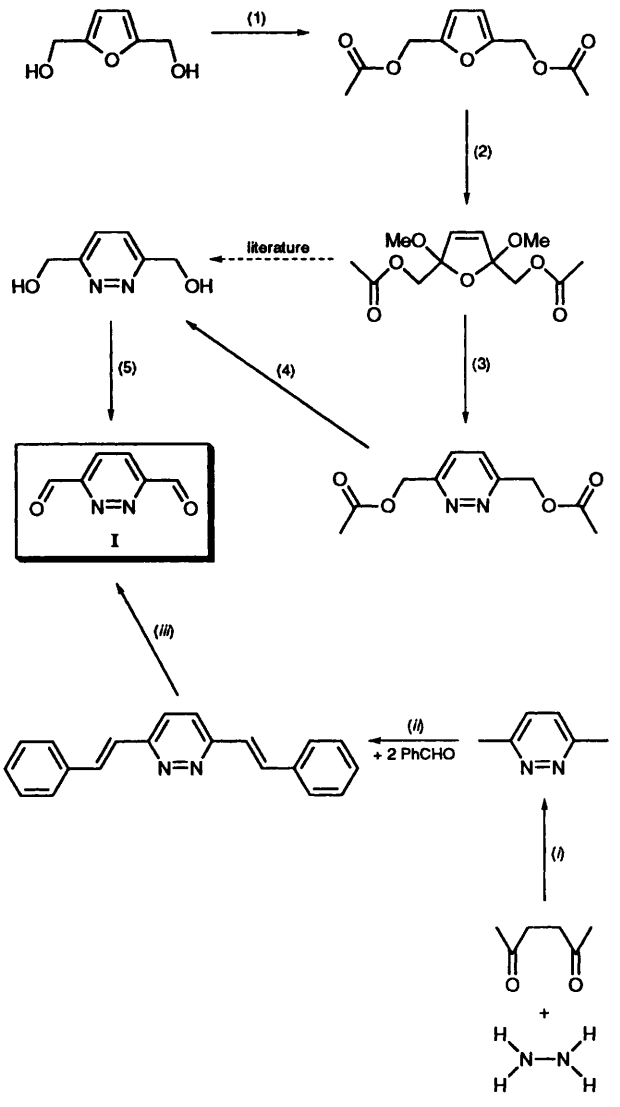
Initially 3,6-bis(hydroxymethyl)pyridazine was prepared from 2,5-bis(hydroxymethyl)furan by the route referenced by Bremard and co-workers[1] (Scheme 1). In our hands step (3) resulted in the isolation of 3,6-bis(acetoxymethyl)pyridazine, not the reported 3,6-bis(hydroxymethyl)pyridazine, so a hydrolysis step was added to the procedure [step (4)]. Bremard and co-workers[1] employed a Swern oxidation in dimethyl sulfoxide (dmso) for the final step, the oxidation of 3,6-bis(hydroxymethyl)pyridazine to 3,6-diformylpyridazine **I**, and then treated **I** *in situ* to form the desired ligands. We successfully performed step (5) by MnO_2 oxidation in dioxane and could therefore readily isolate **I**.

However, in addition to steps (1)–(5) resulting in a lengthy synthesis, the success of step (2) was found to be variable. We therefore adopted the relatively short and attractive synthesis described by Wiley[11] [Scheme 1, steps (*i*)–(*iii*)]. Both starting materials in this synthesis, acetonylacetone and hydrazine hydrate, are cheap and readily available. Steps (*i*) and (*ii*) are both simple and high yielding, and after some slight modifications we found the third and final step of this route to be entirely reliable, providing compound **I** in acceptable yield and purity. Storage of **I** under a nitrogen atmosphere and in a freezer is necessary, in air at room temperature samples decompose significantly overnight to yield a greenish, somewhat oily product.

Macrocyclic complexes

Schiff-base macrocycles are readily formed from compound **I** and 1,3-diaminopropane by template methods. When lead(II) ions are used as templates two different macrocycle sizes can be isolated depending on the reaction conditions employed. Specifically, a 1:1:1 ratio of **I**:1,3-diaminopropane:lead(II) perchlorate resulted in the formation of $Pb_2L^1(ClO_4)_4$ **1** whereas a 2:2:1 ratio gave $[Pb_2L^2][ClO_4]_4$ **2**. In both cases the complexes were obtained in good yield and purity. No evidence for the presence of solvent molecules was found by elemental analysis. The infrared spectra showed the presence of imine bonds and the absence of amine and carbonyl bonds, thus confirming that cyclisation had occurred.

The ability of the same metal salt to template two different macrocycle ring sizes efficiently, in this case lead(II) perchlorate and L^1 *vs.* L^2 macrocycles, simply by employing different reagent ratios, is unprecedented to our knowledge. In previous studies a given metal salt has templated the formation of only one specific macrocycle ring size, so to obtain a macrocycle of different size quite different reaction conditions had to be employed, for example a different template ion or a different anion.[8,12,13] In our two preparations the solvent mixture and the concentrations of the dicarbonyl and diamine components are identical. When the lead-ion concentration is stoichiometric for $[Pb_2L^2]^{4+}$ formation complex **2** slowly precipitates from the reaction solution, in 66% yield, over the 3d it is left to stand.



Scheme 1 Synthesis of 3,6-diformylpyridazine **I** from 2,5-bis(hydroxymethyl)furan [steps (1)–(5)] or from acetonylacetone and hydrazine hydrate [steps (*i*)–(*iii*)]. Reagents and conditions: (1), acetic anhydride–pyridine; (2), Br_2–MeOH; (3), 1% acetic acid–MeOH–$H_2NNH_2{\cdot}H_2O$; (4), activated Amberlite IRA400 resin–MeOH; (5), oxalyl chloride–dmso or MnO_2–dioxane; (*i*), Pd/C–benzene; (*ii*), $ZnCl_2$; (*iii*), O_3–MeOH

No formation of the $[Pb_2L^1]^{4+}$ macrocyclic product **1** is observed. However, on doubling the lead(II) ion concentration (and hence molar ratio to the other reagents) only a small amount of **2** is formed as the equilibrium now favours the alternative product **1**, which is isolated in 60% yield by reducing the solvent volume.

In the absence of added reagents no interconversion between complexes **1** and **2** is observed. However, when **I** and 1,3-diaminopropane are added to **1** ring expansion to the $[Pb_2L^2]^{4+}$ product **2** is observed. Likewise, the reverse reaction, addition of lead(II) ions to **2**, leads to ring contraction and formation of the $[Pb_2L^1]^{4+}$ product **1**. Hence the product is simply determined by the reagent ratios employed, and is due to the effect these ratios have on the position of the product equilibrium $\mathbf{1} + \mathbf{1} \rightleftharpoons \mathbf{2} + 2Pb^{II}$. At high dialdehyde–diamine to lead(II) ratios the equilibrium favours $[Pb_2L^2][ClO_4]_4$ **2** where all of the lead(II) ions present can be wrapped up by the large macrocycle, whereas at low ratios $Pb_2L^1(ClO_4)_4$ **1** is favoured over a mixture of **2** and solvated lead(II) ions. We are not aware of any other examples of such a delicate thermodynamic balance allowing the isolation of two different Schiff-base macrocycle ring sizes.

Transmetallation of $[Pb_2L^2][ClO_4]_4$ **2** with 4 equivalents of manganese(II) perchlorate and an excess of NaSCN led to the formation of $[Mn_2L^1(NCS)_4]$ **3**. The same product was also obtained by an analogous transmetallation of $Pb_2L^1(ClO_4)_4$ **1**. The infrared spectrum showed no evidence of unreacted carbonyl or amine, but rather the presence of imine bonds and inequivalent thiocyanate ions (2078, 2063, 2052, 1987 cm^{-1}). The band below 2000 cm^{-1} is characteristic of single-atom > NCS bridging.[14]

Crystal structures

No crystals of complex **1** have been obtained to date so the macrocycle conformation and the geometry about the lead ions is as yet unknown. However, **2** crystallises well and we have previously reported that the structure determination revealed a dilead(II) complex of the L^2 macrocycle (Fig. 1).[9] Since nearly all of the scattering power corresponded to a higher symmetry (4/*mmm*) the interpretation of the X-ray data was difficult, but a Fourier-difference electron density synthesis gave no evidence that the structure could be interpreted as a disordered L^1 structure.

Single crystals of $[Mn_2L^1(NCS)_4]$ **3** were obtained from evaporation of the reaction solution and the crystal structure determined (Fig. 2, Table 1). This revealed that on transmetallation the macrocycle ring had contracted from (4 + 4) to (2 + 2). The resulting dimanganese(II) complex of L^1 binds a total of four thiocyanate ions in an unsymmetrical manner. All bind *via* the nitrogen atom only, three in a terminal fashion whilst the fourth bridges the two manganese(II) ions as predicted from the analysis of the infrared spectrum. Atom Mn(1) is seven-co-ordinate, binding three thiocyanate ions, whereas Mn(2) is six-co-ordinate with only two co-ordinated thiocyanate ions. Irregular geometries are observed for both atoms, a feature not uncommon in manganese(II) chemistry.[3,13,15] Each manganese atom binds strongly to two thiocyanate groups [Mn(1) to N(40) and N(50), and Mn(2) to

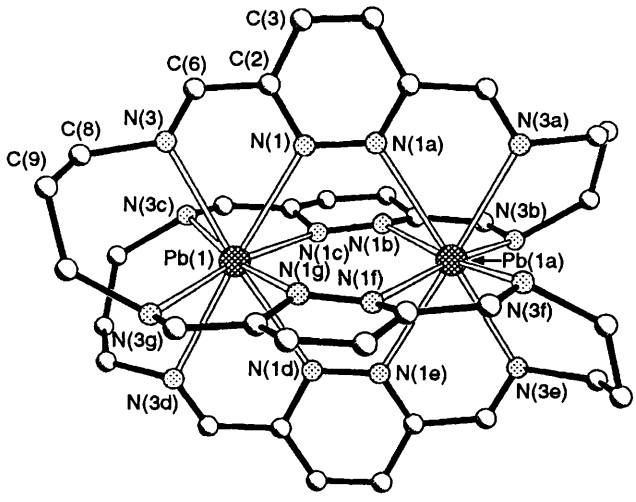


Fig. 1 Perspective view of the cation of complex **2**, $[Pb_2L^2]^{4+}$

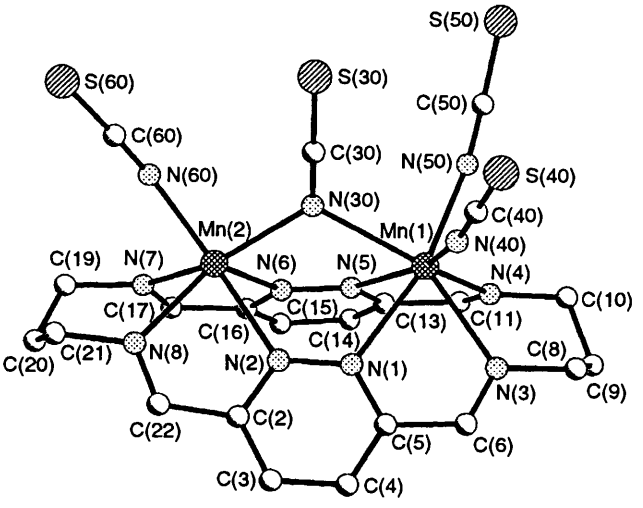


Fig. 2 Perspective view of $[Mn_2L^1(NCS)_4]$ **3**

Table 1 Selected bond lengths (Å) and angles (°) for complex **3**

Mn(1)–N(50)	2.141(5)	Mn(1)–N(40)	2.155(5)
Mn(1)–N(4)	2.337(5)	Mn(1)–N(3)	2.351(5)
Mn(1)–N(1)	2.384(5)	Mn(1)–N(30)	2.417(5)
Mn(1)–N(5)	2.460(5)	Mn(2)–N(60)	2.108(5)
Mn(2)–N(30)	2.193(5)	Mn(2)–N(7)	2.247(5)
Mn(2)–N(8)	2.257(5)	Mn(2)–N(6)	2.288(4)
Mn(2)–N(2)	2.338(5)	Mn(1) · · · Mn(2)	3.904(5)
N(50)–Mn(1)–N(40)	86.5(2)	N(50)–Mn(1)–N(4)	79.7(2)
N(40)–Mn(1)–N(4)	133.0(2)	N(50)–Mn(1)–N(3)	124.7(2)
N(40)–Mn(1)–N(3)	79.0(2)	N(4)–Mn(1)–N(3)	73.0(2)
N(50)–Mn(1)–N(1)	164.9(2)	N(40)–Mn(1)–N(1)	89.7(2)
N(4)–Mn(1)–N(1)	113.2(2)	N(3)–Mn(1)–N(1)	68.6(2)
N(50)–Mn(1)–N(30)	86.9(2)	N(40)–Mn(1)–N(30)	85.3(2)
N(4)–Mn(1)–N(30)	137.6(2)	N(3)–Mn(1)–N(30)	143.2(2)
N(1)–Mn(1)–N(30)	78.3(2)	N(50)–Mn(1)–N(5)	100.0(2)
N(40)–Mn(1)–N(5)	160.0(2)	N(4)–Mn(1)–N(5)	67.0(2)
N(3)–Mn(1)–N(5)	111.5(2)	N(1)–Mn(1)–N(5)	79.2(2)
N(30)–Mn(1)–N(5)	76.2(2)	N(60)–Mn(2)–N(30)	90.4(2)
N(60)–Mn(2)–N(7)	89.4(2)	N(30)–Mn(2)–N(7)	144.6(2)
N(60)–Mn(2)–N(8)	92.7(2)	N(30)–Mn(2)–N(8)	136.2(2)
N(7)–Mn(2)–N(8)	79.2(2)	N(60)–Mn(2)–N(6)	133.1(2)
N(30)–Mn(2)–N(6)	83.9(2)	N(7)–Mn(2)–N(6)	70.9(2)
N(8)–Mn(2)–N(6)	122.7(2)	N(60)–Mn(2)–N(2)	141.6(2)
N(30)–Mn(2)–N(2)	80.6(2)	N(7)–Mn(2)–N(2)	119.0(2)
N(8)–Mn(2)–N(2)	70.3(2)	N(6)–Mn(2)–N(2)	83.2(2)
C(30)–N(30)–Mn(2)	125.1(4)	C(30)–N(30)–Mn(1)	118.8(4)
Mn(2)–N(30)–Mn(1)	115.7(2)	N(30)–C(30)–S(30)	179.4(5)
C(40)–N(40)–Mn(1)	165.6(5)	N(40)–C(40)–S(40)	176.6(5)
C(50)–N(50)–Mn(1)	166.7(5)	N(50)–C(50)–S(50)	176.0(5)
C(60)–N(60)–Mn(2)	157.0(5)	N(60)–C(60)–S(60)	177.3(5)

N(60) and N(30)] thus the bridging thiocyanate is not equally shared but rather is bound more tightly to the six-co-ordinate manganese atom [Mn(1)–N(30) 2.417(5) *vs.* Mn(2)–N(30) 2.193(5) Å]. Likewise the Mn(2)–N(60) bond is shorter than either Mn(1)–N(40) or Mn(1)–N(50). This trend is also observed in the bonds from the macrocycle donor atoms to the manganese atoms; those to the six-co-ordinate manganese atom (2.247–2.338 Å) are significantly shorter than the equivalent bonds to the seven-co-ordinate manganese atom (2.337–2.460 Å). The expansion of the co-ordination sphere of Mn(1) from six- to seven-co-ordinate is presumably due to a delicate balance of ligand-field effects, such that this d^5 ion achieves a slightly greater stability with seven donor atoms at slightly greater distances than it does with six at shorter distances. It is, however, possible that in the reaction solution **3** is in equilibrium with complexes of other co-ordination numbers, and that pure **3** is simply obtained due to draining the equilibrium mixture (**3** is neutral, non-ionic and relatively insoluble). Seven-co-ordination is not unusual for Mn^{II}, being commonly observed when a polydentate ligand constrains donor atoms to make acute angles at the d^5 ion.[13,15] The polydentate (2 + 2) macrocycle is bent; the mean planes through the two pyridazine rings intersect each other at 81.1° and the two manganese atoms lie close to both of these planes (maximum deviation from either plane is 0.22 Å). Each manganese atom therefore occupies the apex of an approximate square pyramid formed by its four macrocycle donor atoms. This leaves a whole side of Mn(1) available to accommodate the three thiocyanate donor atoms. The macrocycle donor–Mn(1)–macrocycle donor angles (67.0, 68.6, 73.0 and 79.2°) are much less than the 90° which would be expected for octahedral co-ordination. Restricted bite angles are also observed at Mn(2) (70.3, 70.9, 79.2 and 83.2°) although in keeping with the observation of shorter bonds to Mn(2) the angles are slightly larger than those at Mn(1) [Mn(1) is 1.33 Å above its (macrocyclic $N)_4$ plane whereas Mn(2) is 1.13 Å above its corresponding plane].

The molecules pack together to form an array of S · · · H–C hydrogen bonds. In addition, π–π interactions are observed between the pyridazine rings in adjacent centrosymmetrically related complexes, resulting in the formation of chains of π-stacked molecules. The stronger of these interactions occurs between adjacent N(5) pyridazine rings, which are parallel to and 3.54–3.58 Å from each other.

Ring contraction during transmetallation

Ring contractions and expansions during transmetallation reactions are well known in Schiff-base macrocyclic chemistry due to the facile hydrolysis/formation of the Schiff-base bonds *in situ*.[13] Reduction of the imine bonds to stable amine bonds is the simplest and most common way of stopping this interconversion. Attempts to reduce $[Pb_2L^2][ClO_4]_4$ **2** to form the octaamine analogue are underway.

Conclusion

The ability to prepare and isolate compound **I** readily has opened up a new class of Schiff-base macrocycles. This has been demonstrated by the successful preparation of the pyridazine-bridged macrocyclic complexes $Pb_2L^1(ClO_4)_4$ **1** $[Pb_2L^2][ClO_4]_4$ **2** and $[Mn_2L^1(NCS)_4]$ **3**. Unprecedented control of macrocycle ring size by the template ion stoichiometry has been observed in the formation of **1** and **2**. Transmetallations of **2** with other transition-metal ions have been carried out and will be the subject of further papers.[9]

Experimental

Acetonitrile (CaH_2), methanol (Grignard) and dioxane (Na) were dried before use. Chloroform was washed with water and dried with Na_2CO_3 before use. Amberlite IRA400 resin (Aldrich) was activated prior to use by washing with 5% NaOH then with water until the washings obtained were neutral. 2,5-Bis(hydroxymethyl)furan was obtained from Aldrich. 3,6-Bis(acetoxymethyl)pyridazine (see discussion above)[1] and 3,6-distyrylpyridazine[11] were prepared by the literature methods. Elemental analyses (C, H, N, S) were performed by the Campbell Microanalytical Laboratory, University of Otago. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer and NMR spectra on a Varian Gemini 200 MHz spectrometer. **CAUTION**: Whilst no problems were encountered in the course of this work both ozonolysis mixtures and perchlorate salts are potentially explosive and should therefore be handled with care.

Preparations

3,6-Bis(hydroxymethyl)pyridazine. 3,6-Bis(acetoxymethyl)pyridazine (0.394 g, 1.76 mmol) was dissolved in methanol (100 cm^3) and Amberlite IRA400 resin (2.5 cm^3) added. The resulting mixture was stirred for 100 min, the resin filtered off, and the solvent removed *in vacuo* to yield a dark brown solid which was used in the next step without further purification (0.178 g, 33%).

3,6-Diformylpyridazine I. *Method A.* A fine suspension of 3,6-bis(hydroxymethyl)pyridazine (0.100 g, 0.714 mmol) in dioxane (50 cm^3) was heated to 90 °C and activated MnO_2[16] (1.00 g) added. The black mixture was refluxed for 30 min before filtering whilst hot. The solvent was removed *in vacuo* to give compound **I** as a yellow crystalline solid (0.047 g, 48%).

Method B. Finely ground 3,6-distyrylpyridazine (2 g, 7 mmol) was suspended in methanol (200 cm^3) and the mixture cooled to *ca.* −50 °C in an acetone–solid CO_2 bath. This temperature was maintained while ozone was bubbled through until the solution clarified and the characteristic pale blue colour of dissolved ozone appeared (60–90 min). The excess of ozone was displaced by bubbling nitrogen through the solution until it became pale yellow. Then a freshly prepared solution of 23% $Na_2S_2O_5$ (12 cm^3) was added dropwise causing the formation of a white precipitate. The mixture was allowed to warm to room temperature whilst still under a nitrogen atmosphere. While this was warming up the ozonolysis was repeated with 2 g of 3,6-distyrylpyridazine. The two resulting methanol suspensions were then combined and filtered. The white solid was washed with methanol (2 × 10 cm^3). Methanol was then removed from the filtrate under vacuum (10 mmHg, *ca.* 1333 Pa) at room temperature until an oily residue remained. The bright yellow oil was promptly rinsed into a separatory funnel with saturated NaCl solution (3 × 15 cm^3) and extracted with diethyl ether (3 × 150 cm^3) to remove the benzaldehyde by-product and the remaining methanol. The aqueous layer was then extracted with chloroform (3 × 150 cm^3) before being continuously extracted with chloroform overnight. The resulting yellow-orange chloroform extracts were combined, dried over Na_2CO_3, and the solvent removed at room temperature *in vacuo*. The yellow solid was used without further purification. A further crop could be obtained from a second overnight continuous extraction with chloroform. The resulting brown-yellow solid was purified by sublimation under high vacuum at 40 °C. It is necessary to store compound **I** (1.224 g, 64%) under a nitrogen atmosphere in a freezer (Found: C, 53.0; H, 2.8; N, 20.6. $C_6H_4N_2O_2$ requires C, 52.9; H, 3.0; N, 20.6%). IR (KBr disc): 3139w, 3110w, 3079w, 3052m, 2863m, 1709s, 1570m, 1554m and 1353m cm^{-1}. δ_H(200 MHz; $CDCl_3$, standard $SiMe_4$) 10.52 [2 H, s, H(6)] and 8.23 [2 H, s, H(3)]. δ_C 191.04 [C(6)], 155.96 [C(2)] and 125.37 [C(3)].

$Pb_2L^1(ClO_4)_4$ 1. 3,6-Diformylpyridazine (0.5 g, 3.68 mmol) was dissolved in a mixture of methanol (180 cm^3) and

acetonitrile (70 cm^3). To this pale yellow solution was added a methanol (20 cm^3) solution of lead(II) perchlorate (1.690 g, 3.68 mmol). 1,3-Diaminopropane (0.272 g, 3.68 mmol) in methanol (20 cm^3) was added dropwise to the stirred clear yellow solution causing a pale precipitate to form. After 4 h the solid had redissolved and the yellow solution was stirred for 3 d after which time a small amount of pale yellow solid had formed. This was filtered off, dried *in vacuo* and subsequently shown to be $[Pb_2L^2][ClO_4]_4$ **2** (0.295 g, 21%). The filtrate was reduced *in vacuo* to a volume of *ca.* 20 cm^3, cooled in an ice-bath, and the resulting solid filtered off and dried *in vacuo*. The pale beige solid was purified by ether diffusion into an acetonitrile solution to yield pure **1** (1.288 g, 60%) (Found: C, 18.5; H, 1.7; N, 9.4. $C_{18}H_{20}Cl_4N_8O_{16}Pb_2$ requires C, 18.6; H, 1.7; N, 9.7%). IR (KBr disc): 3063m, 2922m, 2861m, 1643s, 1617m, 1581m, 1550m, 1097s (br) and 630s cm^{-1}.

$[Pb_2L^2][ClO_4]_4$ 2. This was prepared as above except that the quantities used were: 3,6-diformylpyridazine (0.331 g, 2.43 mmol) in a mixture of methanol (120 cm^3) and acetonitrile (45 cm^3); lead(II) perchlorate (0.561 g, 1.22 mmol) in methanol (10 cm^3); 1,3-diaminopropane (0.180 g, 2.43 mmol) in methanol (20 cm^3). Again, after 4 h the initial solid had redissolved. The yellow solution was then stirred for 3 d over which time complex **2** formed as a pale yellow solid which was filtered off and dried *in vacuo* (0.607 g, 66%) (Found: C, 28.7; H, 2.8; N, 14.3. $C_{36}H_{40}Cl_4N_{16}O_{16}Pb_2$ requires C, 28.7; H, 2.7; N, 14.9%). IR (KBr disc): 3285m (br), 3063m, 2924m, 2860m, 1647s, 1585m, 1551m, 1098s (br) and 623s cm^{-1}.

$[Mn_2L^1(NCS)_4]$ 3. Complex **2** (0.302 g, 0.20 mmol) was dissolved in refluxing acetonitrile (100 cm^3) and $Mn(ClO_4)_2 \cdot 6H_2O$ (0.304 g, 0.84 mmol) in acetonitrile (10 cm^3) was added dropwise to the golden-yellow solution. The resulting slightly darker yellow solution was refluxed for 2 h then NaNCS (0.194 g, 2.40 mmol) in acetonitrile (10 cm^3) added dropwise. A mustard solid formed immediately. After refluxing overnight the mixture was allowed to cool to room temperature and filtered to remove a large quantity of insoluble lead salts. The golden-yellow filtrate was left to evaporate slowly. After 2 weeks the orange-red crystals of complex **3** were filtered off and dried *in vacuo* (0.071 g, 25%) (Found: C, 37.8; H, 2.5; N, 24.1; S, 18.3. $C_{22}H_{20}Mn_2N_{12}S_4$ requires C, 38.0; H, 2.9; N, 24.3; S, 18.6%). IR (KBr disc): 3046m, 3029m, 2927m, 2913m, 2856m, 2078s, 2063s, 2052s, 1987s, 1641m, 1576w and 1552w cm^{-1}. *m/z* 632. $[Mn_2L^1(NCS)_3]^+$.

X-Ray crystallography

Data for complex **3** were collected on a Siemens P4 four-circle diffractometer at 130 K using graphite-monochromated Mo-Kα radiation (λ = 0.710 13 Å).

Crystal data. $C_{22}H_{20}Mn_2N_{12}S_4$, golden-orange rod, crystal dimensions 0.6 × 0.2 × 0.2 mm, triclinic, space group $P\bar{1}$, a = 8.603(5), b = 12.141(6), c = 13.686(5) Å, α = 93.94(4), β = 96.33(4), γ = 99.18(4)°, U = 1397.1(12) $Å^3$, μ = 1.24 mm^{-1}, Z = 2, D_c = 1.642 g cm^{-3}, $F(000)$ = 700.

The unit cell parameters were determined by least-squares refinement of 15 accurately centred reflections ($6 < 2\theta < 22°$). Using 1.4° ω scans at a fixed scan rate of 12° min^{-1}, 5373 reflections were collected in the range $4 < 2\theta < 48°$. Crystal stability was monitored by recording three check reflections every 97 and no significant variations were observed. The data were corrected for Lorentz-polarisation effects and an empirical absorption correction was applied based on ψ-scan data (T_{min} = 0.54, T_{max} = 0.91, SHELXA [17]). The 4387 independent reflections were used to solve the structure by direct methods (SHELXS 86[18]) which resulted in the location of all of the non-hydrogen atoms. The refinement was carried out against all F^2 data (SHELXL 93).[19] All non-hydrogen atoms were anisotropic, and hydrogen atoms were inserted at calculated positions riding on the atoms to which they were attached (including isotropic thermal parameters which were equal to 1.2 times the equivalent isotropic displacement parameter for the attached non-hydrogen atom). The refinement of 361 parameters converged to $R1$ = 0.0509 [for 2912 reflections having $F > 4\sigma(F)$], $wR2$ = 0.0962 and goodness of fit 1.05 (for all 4387 F^2 data). The function minimised in the F^2 refinements was $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, where $w = [\sigma^2(F_o^2) + 3.4816P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. Maximum, minimum electron densities 0.59, −0.41 e $Å^{-3}$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996; Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/1.

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