# Flexible cofacial binuclear metal complexes derived from $\alpha, \alpha$ -bis(salicylimino)-*m*-xylene<sup>†</sup>

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The tetradentate Schiff-base ligand SIXH<sub>2</sub> (a,a-bis(salicylimino)-*m*-xylene), prepared from salicylaldehyde and *m*-xylylenediamine, forms cofacial binuclear complexes with Pd and Cu. Of the two isomers possible (*trans-syn* and *trans-anti*) for M<sub>2</sub>(SIX)<sub>2</sub>, these complexes crystallize exclusively as the *trans-anti* isomer. In ansolvous Pd<sub>2</sub>(SIX)<sub>2</sub>, the metal-containing planes are approximately parallel, with Pd  $\cdots$  Pd 4.416(1) Å. Pd<sub>2</sub>(SIX)<sub>2</sub> also forms a crystalline solvate, in which the molecules adopt a more open conformation with longer metal–metal distances (5.109(1) and 5.112(1) Å). The M  $\cdots$  M distance is significantly longer in Cu<sub>2</sub>(SIX)<sub>2</sub> (6.653(1) Å), because of conformational changes in the *m*-xylylene moieties and substantial tetrahedral distortion about Cu.

# Introduction

We have been investigating the chemistry of cofacial binuclear transition-metal complexes derived from  $bis(\beta-diketone)^1$  and bis $(\beta$ -ketoenamine)<sup>2</sup> ligands (see Fig. 1). One objective of this work has been to achieve the geometric features of the cofacial diporphyrins<sup>3</sup> with binucleating ligands that are more synthetically versatile. The bis( $\beta$ -ketoenamine) complexes Cu<sub>2</sub>(BBI)<sub>2</sub> and Ni<sub>2</sub>(BBI)<sub>2</sub>, for example (Fig. 1(b)), undergo quasireversible two-electron electrochemical oxidation, whereas the analogous mononuclear complexes are oxidized only irreversibly by one electron.<sup>2</sup> Although we were able to characterize several of these bis( $\beta$ -ketoenamine) complexes, other M<sub>2</sub>(BBI)<sub>2</sub> species have proved more difficult to purify. This difficulty may occur because the prepared complexes consist of several isomers: the possibility of cis and trans arrangements of O and NH groups at each metal leads to a total of five possible isomers for  $M_2(BBI)_2$ . We now report the use of the binucleating Schiff base  $\alpha, \alpha$ -bis(salicylimino)-*m*-xylene, which we call SIXH<sub>2</sub>, in the preparation of cofacial binuclear complexes of palladium and copper; see sketches in Fig. 2. This work has two important advantages over our previous studies of bis(β-ketoenamine) complexes. First, the ligand SIXH<sub>2</sub> is easier to prepare, in that a single condensation reaction introduces both the *m*-xylylene bridging group and the coordinating N atoms. Second, the binuclear complexes  $M_2(SIX)_2$ , which can be formed in only two isomers, show substantially greater flexibility in metal-metal distance and conformation than the  $M_2(BBI)_2$  species.

The binuclear complex most closely related to the present work is  $Cu_2(p-SIX)_2$ , recently prepared by McNelis *et al.* (Fig. 2(b)).<sup>4</sup> As might be expected from the *para* geometry of the bridging groups, this ligand leads to somewhat longer  $Cu \cdots Cu$ distances (*ca.* 7.3 Å) than we find with the *meta* isomer. The two SIX<sup>2-</sup> ligands have also been used to prepare binuclear complexes with a single bridging ligand: a dimanganese complex bridged by the *meta* isomer,<sup>5</sup> and diruthenium complexes bridged by one *p*-SIX<sup>2-</sup> and related ligands.<sup>6</sup> Wayland and coworkers have used a single *m*-xylylene linker to join two Rh(II) porphyrin moieties;<sup>7</sup> this species reacts with methanol to yield a H–Rh–Rh–CH<sub>2</sub>OH product.

<sup>†</sup>Electronic supplementary information (ESI) available: A summary of the structure of solvated Pd<sub>2</sub>(SIX)<sub>2</sub>, and experimental and simulated <sup>1</sup>H NMR spectra for Pd<sub>2</sub>(SIX)<sub>2</sub>. See http://www.rsc.org/suppdata/ dt/b4/b412666a/

# Experimental

## Materials and procedures

Chemicals and solvents were reagent or spectrophotometric grade and were used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker 200- and 400-MHz spectrometers. Cyclic voltammograms were recorded by using either a PAR model 174A Polarographic Analyzer or a Wenking TS70/1 potentiostat with a home-built microcomputer interface. The cell contained Pt working and counter electrodes and an aqueous Ag/AgCl (3 M NaCl) reference electrode. The half-wave potential for the Fc/Fc<sup>+</sup> (Fc = ferrocene) reference redox couple in CH<sub>3</sub>CN (0.1 M (Bu<sub>4</sub>N)(O<sub>3</sub>SCF<sub>3</sub>)<sup>8</sup>) under these conditions was 0.47 V. Microanalyses were performed by Desert Analytics (Tucson, AZ). We prepared mononuclear M(salim-Bz)<sub>2</sub> complexes (Fig. 1(d), R = benzyl; M = Pd, Cu; the free ligand Hsalim-Bz is also known as saddamine)<sup>9</sup> for electrochemical comparisons.

# α,α'-Bis(salicylimino)-*m*-xylene (or *m*-xylylenebis(salicylaldimine)), SIXH<sub>2</sub>

To a benzene solution (250 mL) of *m*-xylylenediamine (5.0 g, 0.035 mol), salicylaldehyde (9.0 g, 0.070 mol) was added dropwise over a period of 45 min. The yellow reaction mixture was stirred for an additional 45 min and then allowed to stand overnight. The precipitate that formed was collected, redissolved in dichloromethane and the resulting solution dried over MgSO<sub>4</sub>, filtered and concentrated. Yellow plate-like crystals formed on standing; yield 11 g (90%). This material was recrystallized from hexane; mp 62 °C. Anal. Calc. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.72; H, 8.13; N, 5.85. Found: C, 75.71; H, 8.13; N, 5.64%. Although the recrystallized ligand was not analytically pure, no impurities were evident in its NMR or mass spectra (parent ion, m/z 344). NMR (in CDCl<sub>3</sub>,  $\delta$ /ppm vs. TMS; lower-case letters represent positions shown in Fig. 2): <sup>1</sup>H,  $\delta$  4.82 (s, 4H, h); 7.3 (m, 12H, aromatic); 8.46 (s, 2H, g); 13.4 (s, 2H, l). <sup>13</sup>C, δ63.1 (h); 118.8 (f); 117.0, 118.6 (c, e); 126.8, 127.1, 129.0, 131.4, 132.3 (b, d, j, k, m); 138.6 (i); 161.0 (a); 165.7 (g). (The preparation and <sup>1</sup>H and <sup>13</sup>C NMR assignments for this compound are similar to those for p-SIXH<sub>2</sub>.<sup>10</sup>)

# Pd<sub>2</sub>(SIX)<sub>2</sub> (1)

A solution of  $(CH_3CN)_2PdCl_2$  prepared by dissolving  $PdCl_2$  (0.51 g, 2.87 mmol) in 250 mL of acetonitrile was added dropwise to a well stirred solution of SIXH<sub>2</sub> (0.996 g, 2.9 mmol) and triethylamine (0.625 g, 6.18 mmol) in CH<sub>3</sub>CN. After *ca*.



Fig. 1 Schiff base and related metal complexes: (a) binuclear  $bis(\beta-diketone)$  complex  $M_2(XBA)_2$ , (b) binuclear  $bis(\beta-ketoenamine)$  complex  $M_2(BBI)_2$ , (c) M(salen), (d)  $M(salim-R)_2$ , (e) and (f) chelating and macrocyclic binuclear complexes derived from 2,6-diformylphenol.



**Fig. 2** Binucleating Schiff bases and their complexes: (a) SIXH<sub>2</sub> and the two possible isomers of  $M_2(SIX)_2$ ; the *trans-anti* isomer predominates in the present work. Letters **a**–**m** denote positions for NMR assignments (see Table 1 and Fig. S1<sup>†</sup>); *a* and *β* are the torsion angles about the N–CH<sub>2</sub> and CH<sub>2</sub>–arene bonds, respectively. (b) *p*-SIXH<sub>2</sub>, as studied by McNelis *et al.*;<sup>4</sup> they also isolated only *trans-anti*-Cu<sub>2</sub>(*p*-SIX)<sub>2</sub>. (c) The *m*-phenylenediamine derivative sal-PDAH<sub>2</sub> and its Cu complex.

30 min, a small amount of yellow precipitate was removed by filtration and the yellow-orange filtrate evaporated to dryness. The residue was stirred with  $CH_2Cl_2$ , the resulting mixture filtered again, and the filtrate evaporated to produce crude  $Pd_2(SIX)_2$ . The complex was obtained in analytically pure, crystalline form by layering a  $CH_2Cl_2$  solution of the crude material with  $CH_3OH$ . Anal. Calc. for  $Pd_2C_{44}H_{36}N_4O_4$ : C, 58.88; H, 4.04; N, 6.24. Found: C, 58.51, H, 3.88, N, 6.30%. <sup>1</sup>H and <sup>13</sup>C NMR spectral data for purified crystalline  $Pd_2(SIX)_2$ , which

has been shown (by X-ray analysis; see below) to have the *transanti* geometry, are presented in Table 1. (Additional resonances with similar coupling patterns, which may be due to small amounts of the *trans-syn* isomer, were visible in some spectra of partially purified  $Pd_2(SIX)_2$ . However, these disappeared on repeated recrystallization; all further experiments reported herein were performed on fully purified *trans-anti* material.) The 'H chemical shifts and coupling constants for resonances **b**–**f**, **g** and **h** were identical (within ±0.01 ppm and ±0.1 Hz,

Table 1 <sup>1</sup>H and <sup>13</sup>C NMR parameters for *trans-anti*-Pd<sub>2</sub>(SIX)<sub>2</sub><sup>a</sup>

		a	b	c	d	e	f	g	h	i	j	k	m
	<sup>1</sup> H $\delta$ /ppm Pattern <sup>2</sup> J/Hz		6.63 dd	6.25 ddd	6.96 ddd	6.35 d (br)		7.44 s (br)	4.00, 5.70 dd (AB) 13.4		7.15 dd	7.29 dt	8.02 s (br)
	<sup>3</sup> J/Hz <sup>4</sup> J/Hz <sup>5</sup> J/Hz		7.9 1.8	6.8, 7.8 1.0	6.8, 8.6 1.8	8.0 <sup>b</sup>					7 3	7 1.5	ь ь
	$^{13}C \delta/ppm$	162.8	134.4	114.7	133.9	119.3	119.6	164.0	63.2	148.6	125.6	127.6	126.8
In (	$CD_2Cl_2$ ; chemic	al shifts ı	s. TMS. I	Lower-case	letters <b>a</b> –m	refer to t	he carboı	n atoms la	beled in Fig.	2 or to th	eir attach	ed hydrog	en atoms. <sup>b</sup> No

resolved.

respectively) in spectra recorded at 200 and 400 MHz. Therefore, second-order effects were judged to be negligible in this region. Chemical shifts ( $\pm 0.02$  ppm) and coupling constants ( $\pm 0.5$  Hz) for resonances **j**-**m** were determined from a homonuclear 2D *J*-resolved spectrum. Observed and simulated 200 MHz<sup>1</sup>H spectra for Pd<sub>2</sub>(SIX)<sub>2</sub> are included as supplementary data.

# Cu<sub>2</sub>(SIX)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (2)

A solution of SIXH<sub>2</sub> (0.904 g, 2.62 mmol) in dichloromethane was shaken vigorously with Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>(aq) (26.2 mmol, prepared from CuSO<sub>4</sub>·5H<sub>2</sub>O and NH<sub>3</sub>(aq)) in a separatory funnel over a 30-min period. The dark violet–brown organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to dryness. The dark residue (*ca.* 1.0 g) was dissolved in dichloromethane and the solution dried, filtered, and layered with ethanol. Dark violet crystals (yield 0.75 g, 70%) were deposited over a period of several days. Anal. Calc. for Cu<sub>2</sub>C<sub>45</sub>H<sub>38</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>2</sub> (Cu<sub>2</sub>(SIX)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>): C, 60.27; H, 4.27, N, 6.25. Found: C, 60.43, H, 4.10, N, 6.10%.

#### X-Ray analyses

Crystals obtained as described above were suitable for X-ray analysis. Because of difficulties encountered initially in solving the structure of  $Pd_2(SIX)_2$  (see below), we experimented with other solvent combinations that might yield the complex in a different crystalline form. We found that a solution of  $Pd_2(SIX)_2$ in CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (9 : 1 v/v) yielded triclinic solvated crystals as well as monoclinic  $Pd_2(SIX)_2$  (1) on layering with pentane. The solvated crystals were extensively twinned; this led to poorer Xray data and refined parameters than in the other two structures. The structures of 1 and 2 are presented in full; a summary of the structure of solvated  $Pd_2(SIX)_2$  is available as ESI.<sup>†</sup>

Diffraction data were collected on a Nonius KappaCCD diffractometer fitted with a Mo-Kα source, a graphite monochromator, and an Oxford Cryostream low-temperature device.

*Crystal data*: Pd<sub>2</sub>(SIX)<sub>2</sub> (1), C<sub>44</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>Pd<sub>2</sub>, M = 897.63, monoclinic, space group  $P2_1/c$  (no. 14), a = 10.6000(10), b = 22.796(3), c = 15.486(2) Å,  $\beta = 102.341(6)^\circ$ , U = 3655.5(8) Å<sup>3</sup>, T = 100 K, Z = 4,  $\mu$ (Mo-K $\alpha$ ) = 1.03 mm<sup>-1</sup>, 93055 reflections measured (with  $\theta < 40.3^\circ$ ), 22828 unique ( $R_{int} = 0.048$ ), which were used in all calculations. Final R = 0.033,  $wR(F^2) = 0.086$ .

Cu<sub>2</sub>(SIX)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>(**2**), C<sub>45</sub>H<sub>38</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>4</sub>, M = 896.82, monoclinic, space group  $P2_1/c$  (no. 14), a = 9.931(5), b = 10.021(5), c = 40.358(19) Å,  $\beta = 93.892(16)^\circ$ , U = 4007(3) Å<sup>3</sup>, T = 120 K, Z = 4,  $\mu$ (Mo-Ka) = 1.24 mm<sup>-1</sup>, 24789 reflections measured (with  $\theta < 26.0^\circ$ ), 7110 unique ( $R_{int} = 0.042$ ), which were used in all calculations. Final R = 0.037,  $wR(F^2) = 0.073$ .

Selected bond distances and angles are given for **1** and **2** in Table 2.

# Pd<sub>2</sub>(SIX)<sub>2</sub> (1)

Initial attempts to solve this structure gave coordinates for Pd1 and Pd2 of approximately (0.17, 0.25, -0.03) and (0.12, 0.25, -0.32) respectively. However, this model was difficult to refine,

Table 2 Selected interatomic distances (Å) and angles (°) for M<sub>2</sub>(SIX)<sub>2</sub>

	$M=Pd\left(1\right)$	$\mathbf{M}=\mathbf{Cu}\left(2\right)$	
M1–O1A	1.9764(9)	1.916(2)	
M1–O1B	1.9749(8)	1.901(2)	
M1–N1A	2.0190(11)	1.964(3)	
M1–N1B	2.0206(10)	1.977(3)	
M2–O2A	1.9757(8)	1.8991(19)	
M2–O2B	1.9843(9)	1.9077(19)	
M2–N2A	2.0187(9)	1.953(3)	
M2–N2B	2.0225(10)	1.958(3)	
O1A-M1-O1B	178.77(4)	149.58(10)	
O1A-M1-N1A	92.64(4)	93.70(11)	
O1A-M1-N1B	87.79(4)	92.84(10)	
O1B-M1-N1A	87.55(3)	92.27(10)	
O1B-M1-N1B	92.05(4)	93.97(10)	
N1A-M1-N1B	178.66(4)	155.47(10)	
O2A-M2-O2B	177.31(4)	151.20(9)	
O2A-M2-N2A	92.42(4)	93.16(9)	
O2A-M2-N2B	87.59(4)	91.55(10)	
O2B-M2-N2A	88.14(3)	92.50(10)	
O2B-M2-N2B	91.91(4)	93.83(9)	
N2A-M2-N2B	178.53(4)	157.65(11)	
	. ,	<pre></pre>	

and the resulting structure showed a surprisingly large number of unreasonable bond distances and angles. Palenik *et al.*<sup>11</sup> have discussed this type of structure, in which the heavy atoms are located near y = 0.25 in space group  $P2_1/c$ . Under these conditions, a two-fold ambiguity (differing by 0.25 in z) exists in coordinates for the heavy atoms derived from the Patterson function. Indeed, when we shifted the starting z coordinates for the two Pd atoms by 0.25, the much more reasonable solution described here was quickly reached.

### $Cu_2(SIX)_2 \cdot CH_2Cl_2(2)$

Refinement of this structure was straightforward.

CCDC reference numbers 247674 (1) and 247675 (2). See http://www.rsc.org/suppdata/dt/b4/b412666a/ for crystallographic data in CIF or other electronic format.

### Results

## Synthesis of ligand and complexes

The preparation of  $\alpha,\alpha$ -bis(salicylimino)xylene, as a mixture of *meta* and *para* isomers, was first reported in 1973.<sup>12</sup> A photochemical study of the pure *meta* isomer was published,<sup>13</sup> but without preparative details. Our procedure for the pure *meta* isomer, from *m*-xylylenediamine and salicylaldehyde in 1 : 2 ratio, is similar to that recently reported by Ha and co-workers<sup>14</sup> Reaction of SIXH<sub>2</sub> with PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> and triethylamine, or with aqueous Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>, affords the binuclear complexes M<sub>2</sub>(SIX)<sub>2</sub>. Small quantities of oligomeric or polymeric materials formed in these reactions were much less soluble and readily removed by filtration. (In contrast, for example, our attempts to prepare  $Ni_2(SIX)_2$  by similar methods gave only insoluble, probably polymeric, powders.)  $Pd_2(SIX)_2$  ordinarily crystallizes in ansolvous monoclinic needles (1); however, if the solvent mixture contains methanol, some of the material crystallizes in a solvated triclinic form (see ESI<sup>†</sup>).

#### Crystal structure analyses

The  $M_2(SIX)_2$  complexes consist of two *trans*-M(salim)<sub>2</sub> complexes joined at the N atoms by *m*-xylylene bridges. Structures for the two possible isomers for  $M_2(SIX)_2$ , *trans-syn* (idealized symmetry  $C_{2h}$ ) and *trans-anti* (idealized symmetry  $D_2$ ), are shown in Fig. 2. The structures reported here contain only the *trans-anti* isomer. NMR spectral data for purified *trans-anti*-Pd<sub>2</sub>(SIX)<sub>2</sub> are discussed below.

Individual *trans-anti*- $M_2(SIX)_2$  molecules have helical chirality, and the two enantiomers can be designated *P* and *M* according to the screw sense of the *m*-xylylene bridging groups.<sup>15</sup> Since the structures are centrosymmetric, they contain equal numbers of the two enantiomers. The *P* enantiomer is shown in the ORTEP drawings in Figs. 3 (Pd) and 4 (Cu).



**Fig. 3** ORTEP drawings of  $Pd_2(SIX)_2$  (1), with ellipsoids at the 50% probability level. (a) Top view, showing orientation of *m*-xylylene bridging groups. (b) Side view, with complete atom numbering scheme.

# (a) Pd<sub>2</sub>(SIX)<sub>2</sub> (1)

The  $Pd_2(SIX)_2$  molecules in 1 (Pd  $\cdots$  Pd 4.416(1) Å; see Fig. 3) are very close to the idealized *trans-anti*-M<sub>2</sub>(SIX)<sub>2</sub> shape of Fig. 2. The immediate coordination environments of the Pd atoms are planar within 0.038(1) Å, and nearly parallel: the dihedral angle between the Pd1–O1A–O1B–N1A–N1B and Pd2–O2A–O2B–N2A–N2B least-squares planes is 4.62(7)°. A



**Fig. 4** ORTEP drawing of Cu<sub>2</sub>(SIX)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>, **2**, with ellipsoids at the 50% probability level.

slightly greater deviation from planarity is evident in the larger  $Pd(salim)_2$  moieties: the two (salim)Pd least-squares planes make angles of 18.34(2) and 8.61(4)° at Pd1 and Pd2, respectively. The larger of these slight distortions is noticeable as a slight saddle shape at Pd1 (see Fig. 3).

The  $Pd_2(SIX)_2$  molecules in 1 are arranged in stacks along c, with short intermolecular contacts ( $Pd1 \cdots Pd2N \ 3.412(1) \ Å$ ) suggesting weak  $\pi$  interactions between adjacent molecules. It is noteworthy that this *inter*molecular  $Pd \cdots Pd$  distance is approx. 1 Å shorter than the intramolecular distance.

# (b) $Cu_2(SIX)_2 \cdot CH_2Cl_2$ (2)

The metal-metal distance in this structure (6.653(1) Å; see Fig. 4) is much larger than that in the Pd complex. There are also several other significant changes in geometry in Cu<sub>2</sub>(SIX)<sub>2</sub>. First, the environment about the Cu atoms is distorted away from square-planar toward tetrahedral: the dihedral angles between the Cu1-O1A-N1A and Cu1-O1B-N1B planes, and between the Cu2-O2A-N2A and Cu2-O2B-N2B planes, are 38.2(1) and  $35.7(1)^{\circ}$  respectively. Second, the departure of the two Cu(salim)<sub>2</sub> moieties from parallelism is much greater: the dihedral angle between the Cu1-O1A-O1B-N1A-N1B and Cu2–O2A–O2B–N2A–N2B planes is 62.57(6)°. And finally, the *m*-xylylene bridges in  $Cu_2(SIX)_2$  are turned still farther inward, so that they are almost touching: the closest nonbonded contact between these groups is C11A ··· C11B 3.663(5) Å. This close approach may reflect a weak  $\pi$  interaction between the *m*xylylene groups. (There are also short intermolecular contacts, e.g. 3.381(4) Å between N1A of one molecule and C4A of an adjacent molecule.)

The close intermolecular  $M \cdots M$  contacts observed in 1 are absent in 2. This is most likely because the nonplanar coordination geometry about the Cu atoms in 2 prevents close approach of adjacent metal atoms.

Complex	Reduction	Oxidation	
$\begin{array}{c} Cu_2(SIX)_2\\ Cu(salim-Bz)_2\\ Pd_2(SIX)_2\\ Pd(salim-Bz)_2 \end{array}$	-0.91 -1.37 -1.04 -0.90	1.07 0.76 0.98 > 1.5	

<sup>*a*</sup> Peak potentials (cyclic voltammetry, vs. Ag/AgCl, in CH<sub>3</sub>CN; 1 V s<sup>-1</sup>) for irreversible reduction and oxidation.

# NMR spectra

The <sup>1</sup>H NMR spectrum for crystalline *trans-anti*-Pd<sub>2</sub>(SIX)<sub>2</sub> (1; see Fig. S1, ESI<sup>†</sup>) is well resolved. Assignments of the <sup>1</sup>H and <sup>13</sup>C NMR data were made with use of two-dimensional spectra and homonuclear decoupling experiments. Protons **c** and **d** (see labeling scheme in Fig. 2) appear as partially overlapping eightline patterns (ddd), and proton **b** as a doublet of doublets, due to <sup>3</sup>J(<sup>1</sup>H–<sup>1</sup>H) and <sup>4</sup>J(<sup>1</sup>H–<sup>1</sup>H) coupling. The **e**, **g** and **h** resonances are all noticeably broadened, probably due to weak coupling among them or to N.

# Electrochemistry

Like many of the other binuclear complexes we have studied, the new species M<sub>2</sub>(SIX)<sub>2</sub> are most soluble in halogenated hydrocarbon solvents; they are also slightly soluble in CH<sub>3</sub>CN. Cyclic voltammetry reveals irreversible oxidation and reduction waves for both Cu<sub>2</sub>(SIX)<sub>2</sub> and Pd<sub>2</sub>(SIX)<sub>2</sub>, which are better defined in CH<sub>3</sub>CN than in CH<sub>2</sub>Cl<sub>2</sub>. (We found no sign of chemical reversibility in these waves at scan rates up to 20 V s<sup>-1</sup>, in either solvent.) Table 3 lists peak potentials for the  $M_2(SIX)_2$ complexes and for the mononuclear analogs M(salim-Bz)<sub>2</sub> (Fig. 1(d),  $R = PhCH_2$ ). The best-defined new feature in the binuclear complexes is the oxidation of  $Pd_2(SIX)_2$ , which is at least 0.5 V easier than that for Pd(salim-Bz)<sub>2</sub>. This suggests some stabilization of the higher oxidation states (Pd<sup>III</sup>), as we have observed previously in the  $M_2(BBI)_2$  systems.<sup>2</sup> However, we were unable to isolate the oxidized  $Pd_2(SIX)_2$  species by either chemical or electrochemical methods.

The electrochemical waves for  $Cu_2(SIX)_2$ , both in  $CH_3CN$  and  $CH_2Cl_2$ , were also complicated by adsorption. Successive anodic scans, for example, showed gradually shifting peak potentials and currents. After several such scans, the initial voltammogram shape could be restored by polishing the electrode.

We also recorded the cyclic voltammograms of  $Pd_2(SIX)_2$  in the presence of  $Cl^-$  and  $Br^-$ . These experiments were suggested by the work of Ooi and co-workers with  $Pd_2(pyt)_4$  (pytH = 2pyridinethiol).<sup>16</sup> They found more facile oxidation of  $Pd_2(pyt)_4$ in the presence of halide ions  $X^-$ , due to formation of the metal–metal bonded species  $Pd^{III}_2(pyt)_4X_2$ . In contrast, halide ions have no significant effect on the electrochemical oxidation of  $Pd_2(SIX)_2$ . This difference may be due to the fact that the relatively large  $Pd \cdots Pd$  distance in  $Pd_2(SIX)_2$  (compared to 2.677(1) Å for  $Pd_2(pyt)_4$ <sup>16</sup>) makes the formation of Pd–Pd bonds difficult.

# Discussion

## Isomerism in M<sub>2</sub>(SIX)<sub>2</sub> and related complexes

Mononuclear planar Schiff-base complexes  $M(salim-R)_2$  (see Fig. 1(d)) can form both *cis* and *trans* isomers when R = H. Although the *trans* isomer has been assumed for most such complexes,<sup>17,18</sup> we have shown that the configuration at the metal atoms in the closely related binuclear species  $M_2(BBI)_2$  (M = Ni, Pd) is *cis*.<sup>2</sup> Howie and Fay have also separated the *cis* and *trans* isomers of a similar mononuclear Pd complex.<sup>19</sup> On the other hand, for larger substituents R,  $M(salim-R)_2$  must be *trans*; it

was this requirement that we wished to take advantage of in the preparation of  $M_2(SIX)_2$ .

### Comparison with other binuclear complexes

We have studied a variety of  $bis(\beta-diketones)^{20}$  and  $bis(\beta-ketoenamines)^2$  as ligands for cofacial binuclear metal complexes. The SIXH<sub>2</sub> ligand introduced here provides three advantages over the others we have examined. First, SIXH<sub>2</sub> is easy to prepare, requiring only one step from readily available starting materials; it is air-stable and does not hydrolyze readily. Second, the number of isomers possible for the binuclear complexes  $M_2(SIX)_2$  is more limited. And third, the position and orientation of the *m*-xylylene bridging groups in  $M_2(SIX)_2$  leads to greater conformational flexibility than is observed in the other binuclear complexes.

Ligands closely related to SIXH<sub>2</sub> have been used previously to prepare binuclear metal complexes. The structure of  $Cu_2(p-SIX)_2$ <sup>4</sup> shows helical chirality similar to that of the Cu and Pd complexes described here. Although this type of helicity has been exploited more extensively with polypyridine and related ligands,<sup>15</sup> it is also possible with Schiff bases, even when the local coordination environments approach planarity (as in Pd<sub>2</sub>(SIX)<sub>2</sub>).

Other binucleating ligands lead to a *coplanar* environment for the two metal atoms, because they contain OH groups that can bridge two metal atoms on deprotonation. Binuclear complexes of this type, with the general structure shown in Fig. 1(e), have been prepared with various bridging ligands L and substituents X.<sup>21</sup> A similar macrocyclic coplanar binuclear complex<sup>22</sup> is shown in Fig. 1(f). SIXH<sub>2</sub>, on the other hand, cannot chelate to one metal atom, and cannot bridge two close-lying metal atoms effectively; instead, two SIX<sup>2–</sup> ligands can bridge two metal atoms in the desired cofacial manner.

A macrocyclic ligand based on *o*-phenylenebis(salicylimine), with polyether bridging groups, has been shown to form trinuclear complexes.<sup>23</sup> Nickel(II)<sup>24</sup> and cobalt(II)<sup>25</sup> complexes of the bis(Schiff base) ligand 2,6-bis(salicyliminomethyl)pyridine have been reported. This ligand is likely to yield mononuclear complexes by using the central pyridine N atom for coordination, though cofacial binuclear complexes similar to M<sub>2</sub>(SIX)<sub>2</sub> may also be possible. Ha and co-workers prepared Be, Mg and Zn complexes of SIXH<sub>2</sub> and related ligands for electroluminescence applications,<sup>14</sup> but they did not determine the structures of these complexes.

The copper(II) complex of the *m*-phenylenediamine derivative sal-*m*-pdaH<sub>2</sub> (see Fig. 2(c)) is known to be binuclear.<sup>26,27</sup> This complex exhibits helical chirality and a coordination environment about Cu similar to that in Cu<sub>2</sub>(SIX)<sub>2</sub> (the dihedral angle between the Cu(salim) planes in Cu<sub>2</sub>(sal-*m*-pda)<sub>2</sub> is 43.6°), but the *m*-phenylene bridging groups in Cu<sub>2</sub>(sal-*m*-pda)<sub>2</sub> force the Cu atoms considerably farther apart (Cu ··· Cu 7.435(2) Å). Also, the Cu(salim)<sub>2</sub> moieties in the molecule are approximately coplanar rather than cofacial, so that the bridging groups occupy the central portion of the complex between the two Cu atoms. Still larger metal-metal distances, but with similar environments at the two metal atoms, are obtained with the salicylidenes of 4,4′-diaminodiphenyl ether<sup>28</sup> and 4,4′-diaminodiphenylmethane.<sup>29</sup>

Bis(salicylidene) ligands with hydrocarbon bridging groups have been prepared by Hiratani and co-workers<sup>30</sup> and used to synthesize binuclear Ti(IV) oxo complexes. Diplatinum(II) metalloreceptors recently reported by Hanan and co-workers<sup>31</sup> are based on pyridine ligands, but they provide similar internal cavities and are able to bind anions as internal guests.

# Conformations of M<sub>2</sub>(SIX)<sub>2</sub>

The substantial differences in geometry between  $Cu_2(SIX)_2$  and  $Pd_2(SIX)_2$  complexes (see Figs. 3 and 4) are not due to changes in bond distances, which differ only slightly between Cu and Pd. (The largest differences are observed in the M–N and M–O

	Type <sup>a</sup>	$M = Pd\left(1\right)$	$\mathbf{M}=\mathbf{Cu}\left(2\right)$
C7A-N1A-C8A-C9A N1A-C8A-C9A-C10A C13A-C15A-N2A-C16A C12A-C13A-C15A-N2A C7B-N1B-C8B-C9B N1B-C8B-C9B-C10B C13B-C15B-N2B-C16B C12B-C13B-C15B-N2B	α β α β α β	$\begin{array}{r} -109.30(12)\\ -172.94(10)\\ -88.49(12)\\ 127.23(10)\\ -101.65(12)\\ -174.75(11)\\ -79.62(12)\\ 128.81(11)\end{array}$	- 110.8(3) 47.8(4) - 102.2(3) - 75.9(3) - 111.2(3) - 102.3(4) - 109.1(3) 74.5(4)

" Torsion angle about CH<sub>2</sub>–N (a) or CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> ( $\beta$ ) bond; see illustration in Fig. 2.

distances, which are *ca*. 0.05–0.10 Å shorter for Cu than for Pd.) Changes in bond angles at the metal atoms are more important: the tetrahedral distortion in  $Cu_2(SIX)_2$  allows the Cu atoms to be considerably farther apart than the N atoms.

The largest changes are found in the conformations of the N–CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N bridging groups. The *m*-xylylene moiety provides an essentially fixed distance between the CH<sub>2</sub> groups: the C8A ··· C15A and C8B ··· C15B intramolecular distances are between 5.02 and 5.08 Å in 1 and 2. However, the N ··· N distances vary considerably more (N1A ··· N2A and N1B ··· N2B range from 5.20 Å in 1 to 6.37 Å in 2), along with changes in the C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub> torsion angle  $\beta$ ; see Table 4 and Fig. 2.

We have previously discussed the effects of ligand conformation on the ability of *m*-xylylenebis(\beta-diketones) to form cofacial binuclear complexes.<sup>20</sup> A similar analysis, based on the torsion angles at the N-CH<sub>2</sub> (i.e. atoms N1-C8 and C15-N2; designated a) and  $C_6H_4$ -CH<sub>2</sub> bonds (atoms C8-C9 and C13–C15; designated  $\beta$ ) applies here; see labels in Fig. 2. The symmetrical conformation represented by  $a = 90^{\circ}$  (or  $-90^{\circ}$ ) and  $\beta = 0^{\circ}$  (or 180°) is readily accessible for our previous bis( $\beta$ -diketone)<sup>1</sup> and bis( $\beta$ -ketoenamine)<sup>2</sup> complexes (see, for example,  $M_2(XBA)_2$ , Fig. 1(a)); it would probably also be favorable for the trans-syn isomer of M<sub>2</sub>(SIX)<sub>2</sub>. The transanti isomer requires a more twisted orientation of the mxylylene bridging groups. Molecular models suggest that the most symmetrical arrangement of  $M(salim)_2$  planes and *m*xylylene bridges in (P)-trans-anti- $M_2(SIX)_2$ , with full  $D_2$  pointgroup symmetry, would give a and  $\beta$  of approximately -80and 165°, respectively. These values are approached closely in  $Pd_2(SIX)_2$  (1). (The molecules in the crystalline solvated form of  $Pd_2(SIX)_2$  have a somewhat more open conformation, with greater variations in a and  $\beta$ , and Pd · · · Pd distance ca. 5.11 Å; see ESI.<sup>†</sup>) For Cu<sub>2</sub>(SIX)<sub>2</sub> (2), the variations in both a and  $\beta$ are still more severe, with the *m*-xylylene moieties turned so far toward the open side of the complex that they nearly touch each other.

Thus, the  $M_2(SIX)_2$  complexes studied here exhibit substantial conformational flexibility. Some of this flexibility is associated with distortions of the metal coordination environment toward tetrahedral in  $Cu_2(SIX)_2$ . However, even the  $Pd_2(SIX)_2$  molecules in 1 and its solvate (see ESI†), all of which are essentially square-planar at Pd, are noticeably different in conformation and show  $Pd \cdots Pd$  distances that vary by nearly 0.7 Å.

This greater flexibility, compared to the *m*-xylylene-bridged complexes we have studied previously, is due largely to the orientation of the bridges. In  $M_2(NBA)_2$  and  $M_2(BBI)_2$ , for example, the C–C bonds joining the *m*-xylylene groups to the metal chelate moieties point directly toward the metal atoms; combined with the requirement for retaining the cofacial geometry, this leaves only a small range of acceptable conformations. In contrast, the bridges in  $M_2(SIX)_2$  are substantially twisted, and the bonds between the *m*-xylylene and M(salim)<sub>2</sub> moieties do not point directly toward M. As a result, changes in *a* and  $\beta$ 

can lead to much larger displacements in the  $M(salim)_2$  moieties of  $M_2(SIX)_2$  than are possible for  $M_2(BBI)_2$ .

# **Coordination environments**

The d<sup>8</sup> Pd complex **1** shows the expected square-planar geometry, whereas  $Cu_2(SIX)_2$  is significantly distorted toward tetrahedral coordination. Holm and O'Connor<sup>18b</sup> used the dihedral angle  $\theta$  between the two O–M–N planes as an indication of the square planar-tetrahedral geometry change. The values of  $\theta$  at Cu1 and Cu2 in Cu<sub>2</sub>(SIX)<sub>2</sub>, 38.2(1) and 35.7(1)°, are similar to that observed (35.6°) in one of the polymorphs of Cu(salim-C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>.<sup>32</sup> Solid-state geometries of other Cu(salim-R)<sub>2</sub> species range from planar (R = H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>OH, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>, Ph) to more highly distorted (R = CH(CH<sub>3</sub>)<sub>2</sub>, 59.7°,<sup>33</sup> R = C(CH<sub>3</sub>)<sub>3</sub>, 53.6°<sup>34</sup>). This variability in the solid state, even for R groups of similar sizes in Cu(salim-R)<sub>2</sub>, suggests that the planar and non-planar structures are very close in energy. The same is likely to be true in the present case; thus, in solution, Cu<sub>2</sub>(SIX)<sub>2</sub> molecules may interconvert among a variety of conformations.

### Redox reactions

We observed only irreversible waves in cyclic voltammograms of  $M_2(SIX)_2$  and the mononuclear analogs  $M(salim-Bz)_2$  (M = Pd, Cu; see Table 3); thus, it is difficult to draw quantitative conclusions. However, comparisons of the oxidative peak potentials may be chemically useful. First, Pd<sub>2</sub>(SIX)<sub>2</sub> appears to be significantly easier to oxidize than Pd(salim-Bz)<sub>2</sub>. We have previously noted a similar trend in Pd<sub>2</sub>(BBI)<sub>2</sub> and related complexes;<sup>2</sup> both of these may indicate stabilization of the oxidized binuclear complex [Pd211,111]+ by weak metal-metal interaction. Second, the opposite shift occurs in the Cu system, with the binuclear species more difficult to oxidize. This shift may be connected with the significant distortion of  $Cu_2(SIX)_2$ toward tetrahedral geometry: Cu(salim-Bz)<sub>2</sub> is very flexible, so that oxidation to Cu<sup>III</sup> (which would strongly favor squareplanar coordination<sup>35</sup>) is expected to occur readily; in contrast, oxidizing the less flexible  $\mathrm{Cu}_2(\mathrm{SIX})_2$  to a square-planar  $\mathrm{Cu}^{\text{\tiny III}}$ complex would require substantial structural rearrangement.

# Summary

New cofacial binuclear metal complexes have been prepared using the  $\alpha,\alpha$ -bis(salicylimino)-*m*-xylene (SIXH<sub>2</sub>) ligand. The geometry of the M<sub>2</sub>(SIX)<sub>2</sub> complexes is similar to that of the cofacial bis( $\beta$ -diketone) and bis( $\beta$ -ketoenamine) species we have studied previously. However, the new complexes are easier to prepare in isomerically pure form. Also, the orientation of the *m*-xylylene bridging groups allows for substantially greater conformational flexibility in the complexes. Future work in this area includes related complexes with N<sub>4</sub> coordination about the metal atoms, which should undergo more facile redox reactions; and multifunctional analogs of SIXH<sub>2</sub>, for construction of larger supramolecular species.

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