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Metal Complexes Based on Tetrathiafulvalene-Fused π -Extended Schiff Base Ligands – Syntheses, Characterization, and Properties

Jie Qin,^[a] Chen-Xi Qian,^[a] Nan Zhou,^[a] Rong-Mei Zhu,^[a] Yi-Zhi Li,^[a] Jing-Lin Zuo,^{*[a]} and Xiao-Zeng You^[a]

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 $\pi\text{-}\mathrm{Conjugated}$ tetrathiafulvalene (TTF)-based donors with a monoamine moiety, 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-benzodithiol-5-amine (L_a) and 2-(5,6-dihydro[1,3]dithiolo[4,5-b][1,4]dithiin-2-ylidene)-1,3-benzodithiol-5-amine (L_b), have been synthesized. Condensation of the TTF amines with different pyridinecarbaldehydes afforded new TTF-fused $\pi\text{-}\mathrm{extended}$ Schiff base ligands, $L_a\text{-}\mathrm{imine-4-pyr-idyl}$ (L_1), $L_a\text{-}\mathrm{imine-3-pyridyl}$ (L_2), and $L_b\text{-}\mathrm{imine-2-pyridyl}$ (L_3). Four metal complexes based on these Schiff base pyridine ligands, $M(hfac)_2(L)_2$ ($M=Cu^{II}, L=L_1, 4; M=Mn^{II}, L=L_1, 5; M=Cu^{II}, L=L_2, 6;$ hfac = hexafluoroacetylacetonate) and

Introduction

Tetrathiafulvalene (TTF) and its derivatives have received much attention because of their strongly electrondonating and attractive reversible redox properties. With these advantages, they can be used as building blocks for molecular conductors,^[1-2] molecular switches,^[3] and solar energy systems.^[4] However, the preparation of materials that exhibit synergy between two or more properties (multifunctional materials) is still a challenge. In consequence, much effort has been devoted to associate the TTF core with spin-carrier centers through π -conjugated linkages. which may improve the electron mobility along the molecule as well as enhance the stacking interaction by π -orbital overlap.^[5–8] This approach combines the electrochemically active properties of TTF donors with the optical or magnetic properties of transitional metal ions to obtain interesting multifunctional molecular materials. The appropriate linkages or effective bridges are important to link the paramagnetic centers and conduct electrons. A variety of monoor polydentate organic ligands for metal coordination have

 [a] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China Fax: +86-25-83314502 E-mail: zuojl@nju.edu.cn
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 $[\operatorname{Re}(\operatorname{CO})_4(\operatorname{L}_3)][\operatorname{Re}_2(\operatorname{CO})_6\operatorname{Cl}_3]$ (7), have been synthesized and structurally characterized. The ligands in all of the complexes show a near planar structure, and the different coordination modes of the metal ions and relative orientation of the terminal N donors result in a different crystalline organization in the solid state. The absorption spectra and redox behavior of these new compounds have been studied. These paramagnetic complexes are promising building blocks for the construction of multifunctional materials due to their planar structures and inherent redox properties.

been attached to the TTF moiety, and their corresponding electroactive complexes have been reported.^[9–14] Among them, pyridine and bipyridine groups have attracted the most attention due to their well-known coordination ability to different metal ions.^[15–21]

In order to obtain new electroactive complexes with intriguing structures and interesting properties, we have studied several new π -extended Schiff base pyridine ligands with different coordinated orientations. The TTF-based donors with monoamine moieties, 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-benzodithiol-5-amine (La) and 2-(5,6dihydro[1,3]dithiolo[4,5-b][1,4]dithiin-2-ylidene)-1,3-benzodithiol-5-amine (L_b), were chosen for condensation reactions with different pyridylaldehydes. Three TTF-Schiff base ligands, in which the TTF fragment is covalently linked to 4-pyridyl (L₁), 3-pyridyl (L₂), and 2-pyridyl (L₃, Scheme 1), have been synthesized. The coordination abilities of monodentate ligands L_1 and L_2 have been demonstrated. Their reactions with CuII or MnII in the presence of hexafluoroacetylacetonate (hfac⁻) afforded three new metal complexes, $M(hfac)_2(L)_2$ (M = Cu^{II}, L = L₁, 4; M = Mn^{II}, $L = L_1$, 5; $M = Cu^{II}$, $L = L_2$, 6). Unlike L_1 and L_2 , L_3 can adopt a chelating coordination mode. Our previous reports show that chelating ligands based on TTF derivatives are good for the formation of Re^I complexes.^[22] The reaction between L_3 and $Re(CO)_5Cl$ afforded the new Re^I complex $[\operatorname{Re}(\operatorname{CO})_4(\operatorname{L}_3)][\operatorname{Re}_2(\operatorname{CO})_6\operatorname{Cl}_3]$ (7). This paper describes the full characterization of all of the ligands and complexes, and their spectroscopic and electrochemical properties.



Scheme 1. Structures of L_a-L_3 .

Results and Discussion

Synthesis and Characterization

The synthetic pathway is outlined in Scheme 2. The nitro-substituted 1,3-dithiole-2-thione 1 is the key starting material. Although it has been synthesized by a nucleophilic reaction in moderate yield.^[23-24] we describe here a facile approach for the synthesis of 1 in high yield starting from 1,2-dibromo-4-nitrobenzene and potassium trithiocarbonate. Compound 2 was synthesized by a literature method.^[25] The cross-coupling reactions of 2 with 3a and 3b in the presence of triethyl phosphite afforded La and Lb, respectively. The Schiff bases L1-L3 were prepared by the direct condensation of L_a and L_b with the corresponding pyridinecarbaldehyde in moderate yield. Three mononuclear complexes 4-6 were obtained by the coordination of L_1 or L_2 with $M(hfac)_2$ (M = Cu or Mn), whereas the reaction of $Re(CO)_5Cl$ with 1 equiv. of L₃ afforded 7. All of the new ligands and complexes show good solubility in common polar organic solvents such as CH₂Cl₂, CHCl₃, and CH₃CN.

The compounds were characterized by IR, ¹H NMR, and UV/Vis spectroscopy and MS. In their IR spectra, L_a and L_b display typical NH₂ stretching bands at 3328 and 3362 cm⁻¹, whereas in those of L_1 – L_3 , the NH₂ stretching band disappeared and a new band at around 1620 cm⁻¹, which results from the C=N stretching vibration, is observed. For **4–6**, a sharp absorption band of hfac is clearly visible at around 1645 cm⁻¹, and the coordinated C \equiv O stretching bands in **7** are found in the 2100–1880 cm⁻¹ region.

In their ¹H NMR spectra, L_a and L_b exhibit resonances at about 3.65 ppm for the NH₂ proton, and L_1-L_3 show singlets at around 8.56 ppm, which are assigned to the imine CH proton. Compared with L_3 , all of the H signals in the aromatic rings of 7 are shifted by ca. 0.22–0.27 ppm to lower field, which is in agreement with the decrease of electron density around the pyridyl and phenyl units caused by chelation to Re¹.

Crystal Structures

The solid-state structures of L_a , L_b , L_1 , L_2 , and 4–7 were determined by single-crystal X-ray diffraction. The crystal-lographic and data collection parameters are given in Tables 1 and 2; selected bond lengths and angles are listed in Tables 3, 4, 5, 6, and S1.

Orange crystals of L_a and L_b , suitable for X-ray structure analysis, were obtained by slow evaporation of solutions of a mixture of dichloromethane and hexane. Both compounds crystallize in monoclinic systems ($P2_1$ and $P2_1/c$, respectively). L_a has an approximately planar structure except one of the methyl group stretches out of the plane (Fig-



Scheme 2. Synthetic routes to L₁-L₃.

FULL PAPER

	L _a	L _b	L ₁	L ₂
Empirical formula	$C_{12}H_{11}NS_{6}$	$C_{12}H_9NS_6$	$C_{18}H_{14}N_2S_6$	$C_{18}H_{14}N_2S_6$
M _r	361.58	359.56	450.67	450.67
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_{1}/c$	$P2_{1}/c$	$P2_1/c$
<i>a</i> [Å]	7.8668(13)	6.5417(10)	5.8316(7)	5.0109(8)
b [Å]	5.1367(8)	14.206(2)	10.6633(12)	26.163(4)
<i>c</i> [Å]	18.488(3)	16.4475(19)	31.467(4)	15.370(2)
a [°]	90.00	90.00	90.00	90.00
β [°]	94.667(2)	109.515(5)	90.593(2)	97.556(3)
γ [°]	90.00	90.00	90.00	90.00
V[Å ³]	744.6(2)	1440.7(3)	1956.6(4)	1997.6(5)
Ζ	2	4	4	4
$\rho_{\rm c} [\rm g cm^{-3}]$	1.613	1.658	1.530	1.499
F(000)	372	736	928	928
T [K]	291(2)	291(2)	291(2)	291(2)
$\mu(Mo-K_{\alpha}) [mm^{-1}]$	0.902	0.932	0.705	0.690
Index ranges	$-10 \le h \le 10, -6 \le k \le 6,$	$-7 \le h \le 7, -13 \le k \le 17,$	$-7 \le h \le 7, -12 \le k \le 13$	$-5 \le h \le 6, -32 \le k \le 27$
	$-20 \le l \le 23$	$-20 \le l \le 17$	$-38 \le l \le 21$	$-18 \le l \le 18$
GOF (F^2)	1.055	1.069	1.059	1.045
Flack parameters	0.02(15)	_	_	_
$R_1^{[a]}, w R_2^{[b]} [I > 2\sigma(I)]$	0.0460, 0.0902	0.0624, 0.1188	0.0451, 0.0891	0.0573, 0.1076
[a] $R_1 = \Sigma C - F_c /\Sigma$	$F_{\rm o}$. [b] $wR_2 = [\Sigma w (F_{\rm o}^2 - F_{\rm c}^2)]^2$	$(F_{o}^{2})^{1/2}$.		

Table 1. Crystallographic data for L_a-L₂.

Table 2. Crystallographic data for 4–7.

	4	5	6	7
Empirical formula	$C_{46}H_{30}CuF_{12}N_4O_4S_{12}$	$C_{46}H_{30}F_{12}MnN_4O_4S_{12}$	$C_{46}H_{30}CuF_{12}N_4O_4S_{12}$	C ₂₈ H ₁₂ Cl ₃ N ₂ O ₁₀ Re ₃ S ₆
$M_{\rm r}$	1379.00	1370.40	1379.00	1393.71
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	$P2_1/c$	<i>P</i> 1	<i>P</i> 1	Pbca
a [Å]	20.982(13)	9.2030(10)	8.8546(14)	13.8540(11)
<i>b</i> [Å]	8.271(5)	9.8087(10)	9.9736(15)	11.7330(10)
c [Å]	16.794(11)	34.192(4)	16.136(2)	47.050(4)
a [°]	90.00	93.633(2)	78.023(3)	90.00
β[°]	99.442(12)	93.477(2)	78.905(3)	90.00
γ [°]	90.00	114.3620(10)	89.499(3)	90.00
V[Å ³]	2875(3)	2793.2(5)	1367.3(4)	7647.9(11)
Z	2	2	1	8
$\rho_{\rm c} [\rm g \rm cm^{-3}]$	1.593	1.629	1.675	2.421
F(000)	1390	1382	695	5168
$T[\mathbf{K}]$	291(2)	296(2)	296(2)	296(2)
$\mu(Mo-K_a)$ [mm ⁻¹]	0.900	0.772	0.946	10.065
T 1	$-25 \le h \le 24$,	$-10 \le h \le 10$,	$-10 \leq h \leq 8$,	$-17 \le h \le 17$,
Index ranges	$-10 \le k \le 7$,	$-11 \leq k \leq 8$,	$-12 \leq k \leq 7$,	$-14 \le k \le 14,$
	$-20 \le l \le 20$	$-38 \le l \le 40$	$-17 \le l \le 19$	$-58 \le l \le 57$
GOF (F^2)	1.042	1.087	1.175	1.166
$R_1^{[a]}, w R_2^{[b]} [I > 2\sigma(I)]$	0.0514, 0.0903	0.0578, 0.1554	0.0834, 0.2199	0.0457, 0.1122

[a] $R_1 = \Sigma ||C| - |F_c|| / \Sigma F_o|$. [b] $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)]^{1/2}$.

Table 4. Selected bond lengths [[Å]	and	angles	[°]	for 5 .
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Table 3. Selected bond lengths [Å] and angles [°] for 4.				2.273(3) 2.151(3)	Mn(1)-N(4) Mn(1)-O(2)	2.245(4) 2.171(3)
2.012(3)	Cu(1)–O(1)	2.098(3)	Mn(1) - O(3)	2.206(3)	Mn(1) - O(4)	2.171(3) 2.152(3)
2.161(2)	C(3)-C(4)	1.347(5)	C(1) - C(2)	1.332(7)	C(3)–C(4)	1.328(8)
1.299(4)	C(7) - C(8)	1.378(5)	C(5) - C(6)	1.382(6)	C(11) - N(2)	1.134(7)
1.450(4)	C(13)–N(1)	1.241(4)	C(17)–C(18)	1.350(6)	C(19)–C(20)	1.339(6)
85.64(10)	N(2)-Cu(1)-O(1)	90.41(11)	C(21) - C(22)	1.391(6)	C(27) - N(1)	1.246(6)
89.59(11)	N(2)-Cu(1)-O(2)	87.12(11)	O(1)–Mn (1)–O(2)	82.21(11)	O(1)–Mn (1)–O(4)	177.59(12)
92.88(11)	$N(2)-Cu(1)-N(2)^{\#1}$	180.00(15)	O(2)–Mn (1)–O(3)	82.20(12)	O(2)–Mn (1)–O(4)	99.05(12)
124.0(3)	C(14)-C(13)-N(1)	125.2(3)	O(3)–Mn (1)–O(4)	80.97(11)	N(3)-Mn(1)-O(3)	164.09(13)
mations used + 1.	d to generate equival	ent atoms:	N(3)–Mn(1)–N(4) C(12)–C(11)–N(2)	97.13(13) 124.0(6)	N(4)-Mn(1)-O(2) C(28)-C(27)-N(1)	166.61(13) 120.9(5)
	2.012(3) 2.161(2) 1.299(4) 1.450(4) 85.64(10) 89.59(11) 92.88(11) 124.0(3)	$\begin{array}{c cccc} \text{ond lengths [Å] and angles [°] for 4.} \\ \hline 2.012(3) & \text{Cu(1)-O(1)} \\ 2.161(2) & \text{C(3)-C(4)} \\ 1.299(4) & \text{C(7)-C(8)} \\ 1.450(4) & \text{C(13)-N(1)} \\ 85.64(10) & \text{N(2)-Cu(1)-O(1)} \\ 89.59(11) & \text{N(2)-Cu(1)-O(2)} \\ 92.88(11) & \text{N(2)-Cu(1)-N(2)}^{\#1} \\ 124.0(3) & \text{C(14)-C(13)-N(1)} \\ \hline \\ $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 5. Selected bond lengths [Å] and angles [°] for 6.

Cu(1)–N(2)	2.046(6)	Cu(1)–O(1)	2.004(5)
Cu(1)–O(2)	2.282(5)	C(3)–C(4)	1.331(10)
C(5)-C(6)	1.330(9)	C(7)-C(8)	1.393(9)
C(13)-C(14)	1.471(10)	C(12)–N(1)	1.426(8)
C(13)–N(1)	1.238(9)		
O(1)–Cu(1)–O(2)	94.03(19)	N(2)-Cu(1)-O(1)	90.0(2)
N(2)-Cu(1)-O(1) #1	90.0(2)	N(2)-Cu(1)-O(2)	91.3(2)
N(2)-Cu(1)-O(2) #1	88.7(2)	$N(2)-Cu(1)-N(2)^{\#1}$	180.000(1)
C(12)-N(1)-C(13)	122.1(7)	C(14)-C(13)-N(1)	121.4(7)

Symmetry transformations used to generate equivalent atoms: #1: -x, -y + 1, -z.

Table 6. Selected bond lengths [Å] and angles [°] for 7.

2.164(8)	Re(1)–N(2)	2.191(7)
1.933(8)	Re(1)-C(2)	2.006(10)
1.917(12)	Re(1)-C(4)	2.038(12)
2.524(2)	Re(2)Cl(2)	2.510(3)
2.509(2)	Re(3)–Cl(1)	2.537(3)
2.501(2)	Re(3)-Cl(3)	2.508(2)
1.894(12)	Re(2)–C(27)	1.891(12)
1.888(10)	Re(3)–C(23)	1.881(13)
1.892(11)	Re(3)-C(25)	1.898(11)
1.453(14)	C(14)–C(15)	1.393(13)
1.352(15)	C(19)–C(20)	1.342(15)
1.283(12)	C(11)–N(2)	1.444(12)
74.8(3)	N(1)-Re(1)-C(3)	173.4(4)
174.2(4)	C(2)-Re(1)-C(4)	178.1(5)
78.68(8)	C(27)–Re(2)–C(28)	87.6(4)
170.9(3)	Cl(2)-Re(2)-C(26)	174.9(4)
174.4(3)	Cl(1)-Re(3)-Cl(2)	79.88(8)
89.6(5)	Cl(1)-Re(3)-C(25)	171.6(3)
174.2(3)	Cl(3)-Re(3)-C(23)	174.9(3)
83.93(8)	Re(2)-Cl(2)-Re(3)	84.96(8)
84.84(8)		
	$\begin{array}{c} 2.164(8) \\ 1.933(8) \\ 1.917(12) \\ 2.524(2) \\ 2.509(2) \\ 2.501(2) \\ 1.894(12) \\ 1.894(12) \\ 1.892(11) \\ 1.453(14) \\ 1.352(15) \\ 1.283(12) \\ 74.8(3) \\ 174.2(4) \\ 78.68(8) \\ 170.9(3) \\ 174.4(3) \\ 89.6(5) \\ 174.2(3) \\ 83.93(8) \\ 84.84(8) \end{array}$	$\begin{array}{llllllllllllllllllllllllllllllllllll$

ure S1). The average deviation from a least-squares plane through the remaining atoms is 0.0591 Å, whereas for the TTF core alone, it amounts to 0.0441 Å. For L_b (Figure S2), the average deviation from a least-squares plane through all the atoms is 0.1601 Å, and 0.0898 Å for the TTF core alone, which reflects its almost coplanar conformation.



Figures 1 and 2 show the molecular structure of L_1 and L_2 , respectively. For L_1 , the TTF skeleton has a nonplanar boat-like conformation, and the average deviation from the least-squares plane is 0.1669 Å. The dihedral angle between the two five-membered rings (containing S1, S2, S3, and S4) is 20.81(1)°. For L₂, the TTF backbone is nearly planar with a dihedral angle of 2.61(1)° between the two five-membered rings (containing S1, S2, S3, and S4), and the average deviation from a least-squares plane is only 0.0190 Å. The pyridyl ring and phenyl group are not coplanar and the dihedral angles between them are 12.83(1) and 35.49(1)° in L_1 and L_2 , respectively. Due to crystal packing effects, the methyl substituents in the two ligands are arranged in a distinctly out-of-plane conformation. In L1, the two methyl groups point in opposite positions, whereas in L_2 , they are on the same side.

The asymmetric unit of **4** contains one molecule. As shown in Figure 3, the central Cu^{2+} ion lies on the inversion center and adopts a pseudooctahedral coordination environment, which is defined by four oxygen donors from two hfac anions in the equatorial plane. The Cu1–O1 and Cu1–O2 distances are 2.098(3) and 2.161(2) Å, respectively. The *trans* pyridine nitrogen atoms of L₁ occupy the axial positions with a short Cu1–N2 bond length of 2.012(3) Å. The dihedral angle between the pyridyl plane and the acac plane is 80.77(1)°. The Cu–O and Cu–N bond lengths are comparable to those found in the similar complex, *trans*-Cu(hfac)₂(TTF–Py)₂.^[26]

The central C=C bond length of the TTF core is 1.299(4) Å, which is within the normal range for a neutral molecule.^[26–27] In 4, L_1 is not planar, and the TTF backbone is more bent than in the free ligand, which is evidenced by the dihedral angle of 33.33(1)° between the two five-membered rings (containing S3, S4, S5, and S6). The dihedral angle between the coordinated pyridyl unit and phenyl group is 12.01(1)°, which indicates that they are not coplanar. The adjacent molecules are stacked in an overlapping arrangement in a palisade fashion (Figure 4). The shortest intermolecular S···S distance is 3.844 Å (S1···S6).

The ORTEP diagram of 5 is depicted in Figure 5. The Mn^{II} ion lies on a two-fold axis and adopts a distorted octa-



Figure 1. Molecular structure of L_1 (50% probability displacement ellipsoids), front and side views are presented.



Figure 2. Molecular structure of L₂ (50% probability displacement ellipsoids), front and side views are presented.



Figure 3. ORTEP view of 4 with the atom numbering scheme (50% probability displacement ellipsoids, H atoms are omitted for clarity).



Figure 4. Crystal packing of 4 viewed along the c axis (H atoms and hfac⁻ units are omitted for clarity).

hedral coordination geometry. L_1 has a *cis* coordination mode with an N3–Mn1–N4 bond angle of 97.13(13)°, which is different to that in **4**. The Mn–N bond lengths range from 2.245(4)–2.273(3) Å. The average central C=C bond length of the TTF core is 1.341 Å, which is longer than that in **4**. In contrast to **4**, L_1 is almost planar in **5**. The average dihedral angle between the two five-membered rings is 6.43(1)°, and the average dihedral angle between the coordinated pyridyl ring and the phenyl group is 10.26(1)°.

In the solid state, the molecules are stacked in a headto-tail fashion. The shortest intermolecular S···S contact is $3.642 \text{ Å} (S12 \cdot \cdot \cdot S12^{\#2})$, symmetry code: $\#2 - x \cdot 1, -y - 2, -z)$, which is slightly shorter than the sum of the van der Waals radii (3.70 Å) and leads to the formation of dimers. The dimers are aligned side by side along the *c* axis and further connected through S6 · · · S11 contacts (3.633 Å) to give a 1D zigzag chain structure (Figure 6).

The use of 3-pyridine-type L_2 is to control the supramolecular motifs as the relative orientations of the nitrogen donors on the pyridyl rings might result in different building blocks. Crystallization of L_2 with Cu(hfac)₂ from the





Figure 5. ORTEP view of 5 with the atom numbering scheme (50% probability displacement ellipsoids, H atoms are omitted for clarity).



Figure 6. The 1D zigzag chain of 5 formed by short intermolecular S···S interactions (H atoms are omitted for clarity).

same solvent system as **4** afforded **6**. As shown Figure 7, the central Cu²⁺ ion in **6** lies on the inversion center and adopts a pseudooctahedral coordination environment, surrounded by four oxygen atoms from two hfac⁻ ligands and two nitrogen atoms from the pyridine moiety of L₂. The central C=C bond length of the TTF core is 1.330(9) Å. L₂ is almost planar in **6**. In the TTF skeleton, the dihedral angle between the two five-membered rings (containing S3, S4, S5, and S6) is 2.70(1)°. In the solid state, unlike **4**, the molecules of **6** are face-to-face self-assembled to form a 1D chain-like structure along the *c* axis through short π - π stacking interactions [the centroid···centroid distance between benzene rings of adjacent molecules is 3.663(6) Å, Figure 8].

Different from L_1 and L_2 , L_3 prefers a bidentate binding mode for the chelation of transition metal ions. The reaction of L_3 with 1 equiv. of Re(CO)₅Cl afforded 7 in high yield. In previous reports, the common products of reactions between Re(CO)₅Cl and N^{\cap}N ligands (such as 2-pyridinylimine and its derivatives) are Re^I tricarbonyl complexes.^[28–31] As shown in Figure 9, the asymmetric unit in 7 consists of cationic [Re(CO)₄(L₃)]⁺ with [Re₂Cl₃(CO)₆]⁻ [tri-µ-halogenohexacarbonyldirhenate(I)] as the counterion.

In the cation, L_3 coordinates Re(1) by two nitrogen atoms to form a strained five-membered metallacycle. As a result, the pyridyl ring forms a large dihedral angle of 51.70(1)° with the phenyl ring. The average Re1–N bond length is 2.177 Å. The N1–Re1–N2 angle of 74.8(3)° is sig-



Figure 7. ORTEP view of 6 with the atom numbering scheme (50% probability displacement ellipsoids, H atoms are omitted for clarity).



Figure 8. π - π stacking interactions in 6 viewed along the *a* axis (H atoms are omitted for clarity).



Figure 9. ORTEP view of 7 with the atom numbering scheme (50% probability displacement ellipsoids).

nificantly smaller than the ideal value of 90°, which is due to the steric requirement of L₃. The average Re–C (C1 and C3) bond length for the terminal CO groups in the equatorial plane that includes the pyridine–imine ligand is 1.925 Å, which is shorter than the average value for the Re– C (C2 and C4) bond (2.022 Å) in the axial position. All other bond lengths and angles are in good agreement with the related complexes [Re(bpy)(CO)₄](PF₆)^[32] and [Re(bpy)(CO)₄](OSO₂CF₃)^[33] (bpy = 2,2'-bipyridine or its derivatives). The anion consists of two rhenium atoms bridged by three chlorine atoms, and three terminal carbonyl groups complete the octahedral coordination for each rhenium atom. The average Re–Cl distance is 2.515 Å, and the average Re–C distance is 1.891 Å, which is shorter than that in the cation. The Re–C≡O bond angles of 176.5(9)– 177.1(10)° are slightly distorted from linearity. The average angle of Re2–Cl–Re3 is 84.58°. These values agree well with those found in similar complexes.^[34] The Re(2)–Re(3) distance of 3.384(1) Å is too long to postulate a direct metal– metal interaction.

Shorter intermolecular S···S contacts are observed between the cations [S4···S5 3.672(5) Å], which form a 1D chain motif along the *a* axis. The dinuclear rhenium(I) anions are located between the cations (Figure 10).



Figure 10. View of the crystal packing arrangement of 7. The dashed lines represent S···S nonbonded contacts.

Spectroscopic Properties

The absorption spectra of all of the reported compounds were measured in dichloromethane/acetonitrile (1:1) solution at room temperature (Figure 11). The absorption data are summarized in Table 7.



Figure 11. Absorption spectra of L_a , L_b , L_1 – L_3 , and 4–7 in CH₂Cl₂/ CH₃CN (1:1, v/v; $c = 2.0 \times 10^{-5}$ M).

All the ligands exhibit a strong absorption band at high energy ($\lambda < 400$ nm), which is assigned to the intraligand $\pi \rightarrow \pi^*$ transition. Compared with L_a and L_b, L₁-L₃ show



	Absorption, λ	_{abs} [nm] (ε /m ⁻¹ c	m^{-1})	
La	229 (49293)	261 (25959)	328 (10903)	
L _b	225 (32948)	315 (10876)	336 (8307)	
L_1	231 (44649)	258 (28066)	325 (16110)	425 (3408)
L_2	228 (54468)	259 (29895)	325 (17239)	412 (3217)
L_3	226 (68213)	258 (34659)	332 (13777)	410 (2544)
4	235 (44387)	305 (42416)	422 (5412)	
5	233 (41869)	304 (39744)	417 (5674)	
6	232 (41755)	304 (39744)	410 (5506)	
7	230 (55542)	305 (24911)	436 (4021)	

an additional weak broad absorption band at lower energy (400–500 nm), which corresponds to the intramolecular charge-transfer transition from the highest occupied molecular orbital in TTF to the lowest unoccupied molecular orbital in the electron-accepting pyridyl unit.^[35] However, for mononuclear **4–6**, no obvious bands with metal-to-ligand charge transfer (MLCT) character are observed, whereas 7 shows a weak MLCT [$d\pi(\text{Re})\rightarrow\pi^*(\text{L})$] band at around 500–600 nm.

The UV/Vis/NIR spectra of 4–7 were investigated upon addition of the oxidant NOPF₆ in dichloromethane/acetonitrile (1:1) solution (Figure 12). In 4, a characteristic absorption band of TTF is exhibited at 305 nm. Upon the addition of NOPF₆, two characteristic absorption bands of the TTF⁺⁺ species at around 450 and 950 nm are observed.^[36] After further oxidation with NOPF₆, the characteristic band of the dicationic TTF species at around 600 nm is no longer observed. The oxidation experiments were also performed in different solvents, and the results are similar, which suggests that the oxidized compounds can be obtained chemically. Similar phenomena were also observed for **5–7**.



Figure 12. UV/Vis/NIR absorption spectra of 4-7 upon the addition of NOPF₆.

FULL PAPER

Electrochemical Properties

The electrochemical properties were studied by cyclic voltammetry, and the data are collected in Table 8.

Table 8. Summary of redox potentials [V] for $L_a\mathchar`-L_3$ and $4\mathchar`-7$ (vs. Ag/AgNO_3).

	$E_{1/2}^{1}$	$E_{1/2}^{2}$	$E_{\rm p}^{\rm ox}$
La	0.32	0.60	_
L _b	034	0.63	_
L_1	0.43	0.72	_
L_2	0.42	0.71	_
L_3	0.41	0.71	_
4	0.42	0.72	
5	0.42	0.72	
6	0.41	0.74	
7	0.47	0.79	1.38

As shown in Figure 13, L_a , L_b , and L_1-L_3 exhibit the usual two-step reversible single-electron oxidations of TTF derivatives, which are derived from the successive oxidation of the TTF unit to TTF⁺ and TTF²⁺, respectively. The E^{1}_{ox} and E^{2}_{ox} values for L_a and L_b are around 0.33 and 0.61 V, respectively. Compared with the precursors, the electron-withdrawing nature of the pyridine ring through the conjugated bridge makes the oxidation of the TTF core more difficult for L_1-L_3 .^[4a,37] The two redox peaks are positively shifted by 90 and 100 mV, respectively, which also confirms the conjugation through the imine junction.^[38]



Figure 13. Cyclic voltammograms of L_a , L_b , and L_1-L_3 (5 × 10⁻⁴ M) in CH₂Cl₂/CH₃CN (1:1, v/v) with *n*Bu₄NClO₄ (0.1 M) at a sweep rate of 100 mV/s.

In **4–6**, the two observed redox potentials for the TTF core remain almost unchanged (Figure 14). The small effect of complexation on the oxidation potentials can be ascribed to the large separation between the TTF core and the metallic fragment.^[39]



Figure 14. Cyclic voltammograms of 4–7 (5×10^{-4} M) in CH₂Cl₂/ CH₃CN (1:1, v/v) with *n*Bu₄NClO₄ (0.1 M) at a sweep rate of 100 mV/s.

In 7, chelation to the Re^I ion enhances the electron-withdrawing ability of the 2-pyridine ring even further, which causes a decrease of the electron density at the TTF core and results in the large positive shifts of E^{1}_{ox} and E^{2}_{ox} (about 60 and 75 mV, respectively) compared to L₃.^[40] The third irreversible oxidation peak at about 1.36 V is assigned to the Re^I-centered one-electron oxidation process.^[22,41]

Conclusions

A useful synthetic approach for π -extended TTF–Schiff base ligands has been reported. Four coordination complexes based on these redox active ligands have been prepared and structurally characterized. The different coordination modes of the metal ions and relative orientation of the terminal N donors result in the different crystalline organization of the complexes in the solid state. Electrochemical studies confirmed π -electron conjugated structures and interesting redox active properties for all compounds. The results demonstrate that these new imine-bridged TTF ligands that bear diverse substitution patterns are useful for the synthesis and design of new metal complexes. Further work to obtain oxidized complexes that combine magnetic and conducting properties is in progress.

Experimental Section

General Procedures: IR spectra were recorded with a Vector22 Bruker spectrophotometer (400–4000 cm⁻¹) as KBr pellets. UV/Vis spectra were measured with a UV-3100 spectrophotometer. Elemental analyses were performed with a Perkin-Elmer 240C analyzer. NMR spectra were measured with a Bruker AM 500 spectrometer. Mass spectra were determined with an Autoflex II TM instrument for MALDI-TOF-MS, GC-TOF instrument for EI-MS and an LCQ Fleet instrument for ESI-MS. Absorption spectra were measured with a Shimadzu UV-3100 spectrophotometer. Cyclic voltammograms were recorded with an Im6eX electrochemical analytical instrument, with glassy carbon as the working electrode, platinum as the counter electrode, Ag/AgNO3 as the reference electrode, and 0.1 M nBu₄NClO₄ as the supporting electrolyte. All the potentials were run at a scan rate of 100 mV/s. 4,5-Bis(methylthio)-1,3-dithiol-2-thione (3a) and 4,5-ethylenedithio-1,3-dithiol-2-thione (3b) were synthesized according to literature procedures.^[41b]



5-Nitro-1,3-benzodithiole-2-thione (1): A mixture of potassium sulfide (43%, 2.06 g, 8.03 mmol), carbon disulfide (1 mL), and *N*,*N*-dimethylformamide (5 mL) was stirred for 2 h at room temperature. To the red suspension of potassium trithiocarbonate was added 1,2-dibromo-4-nitro benzene (2.10 g, 7.40 mmol), and the mixture was stirred for 32 h at 85 °C. The mixture was poured into water (100 mL), and the precipitate was collected by filtration. The solid was purified by chromatography on silica gel with dichlorometh-ane/petroleum ether (v/v = 1:1) to obtain **1** as a pure yellow solid; yield 1.53 g (93%). IR (KBr): $\tilde{v} = 1564$, 1511, 1338, 1306, 1067, 891, 767, 736 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.35$ (d, J = 1.5 Hz, 1 H), 8.24 (dd, J = 9.0, 2.0 Hz, 1 H), 7.62 (d, J = 9.0 Hz, 1 H) ppm. EI-MS: *m*/*z* (%) = 229.0 (100) [M]⁺, 185.0 (30) [M – CS]⁺. C₇H₃NO₂S₃ (229.29): calcd. C 36.67, H 1.32, N 6.11; found C 36.71, H 1.28, N 6.14.

5-Amino-1,3-benzodithiole-2-thione (2): A solution of SnCl₂·2H₂O (7.80 g, 34.57 mmol) in ethanol (10 mL) was added to a stirring solution of **1** (2.00 g, 8.73 mmol) in HCl (90 mL, 12 M) and ethanol (45 mL), and the mixture was heated to reflux for 13 h. The precipitate was collected by filtration and washed with water. The crude product was purified by silica gel chromatography with dichloromethane/petroleum ether (v/v = 2:1) as an eluent to obtain **2** as a light yellow solid; yield 0.69 g (40%). IR (KBr): $\tilde{v} = 3364$, 1635, 1583, 1464, 1423, 1297, 1242, 1062, 833, 809, 568, 446 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.22$ (d, J = 8.5 Hz, 1 H), 6.77 (d, J = 1.9 Hz, 1 H), 6.72 (dd, J = 8.5, 2.0 Hz, 1 H), 3.88 (s, 2 H) ppm. EI-MS: m/z (%) = 199.0 (100) [M]⁺, 155.0 (42) [M - CS]⁺. C₇H₅NS₃ (199.30): calcd. C 42.18, H 2.53, N 7.03; found C 42.38, H 2.61, N 7.08.

2-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-benzodithiol-5-amine (L_a): Under an argon atmosphere, a solution of **2** (0.40 g, 2.01 mmol), **3a** (0.48 g, 2.28 mmol), and P(OEt)₃ (4.10 mL) in toluene (15 mL) was heated to 120 °C for 4 h. After the reaction, excess solvent was removed under vacuum to afford a red oily residue, which was subjected to silica gel column chromatography with dichloromethane/petroleum ether (v/v = 1:1) as the eluent; yield 26%. Orange crystals suitable for X-ray diffraction were obtained from evaporation of a solution of L_a in dichloromethane and hexane. IR (KBr): \tilde{v} = 3328, 2914, 1584, 1460, 1422, 1298, 1242, 1061, 897, 836, 811, 772, 568, 444 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 6.99 (d, *J* = 7.5 Hz, 1 H), 6.61 (s, 1 H), 6.46 (d, *J* = 8.0 Hz, 1 H), 3.66 (s, 2 H), 2.43 (s, 6 H) ppm. MS (MALDI-TOF): *m/z* = 361.1 [M]⁺. C₁₂H₁₁NS₆ (361.61): calcd. C 39.86, H 3.07, N 3.87; found C 39.82, H 3.09, N 3.94.

2-(5,6-Dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-1,3-benzodithiol-5-amine (L_b): L_b was obtained according to the procedure reported above for L_a by using 3b instead of 3a. Orange crystals suitable for X-ray diffraction were obtained from evaporation of a solution of L_b in dichloromethane and hexane; yield 34%. IR (KBr): $\tilde{v} = 3362$, 2919, 1609, 1586, 1463, 1283, 1120, 884, 840, 802, 771, 421 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): $\delta = 6.98$ (d, J =8.5 Hz, 1 H), 6.60 (s, 1 H), 6.46 (d, J = 8.5 Hz, 1 H), 3.64 (s, 2 H),3.27 (s, 4 H) ppm. MS (MALDI-TOF): m/z = 359.1 [M]⁺. C₁₂H₉NS₆ (359.60): calcd. C 40.08, H 2.52, N 3.89; found C 40.12, H 2.47, N 3.93.

L_a-Imine-4-pyridyl (L₁): A mixture of **L**_a (0.12 g, 0.33 mmol), pyridine-4-carbaldehyde (32 μ L), and a catalytic amount of formic acid in distilled ethanol (15 mL) was heated to reflux. After stirring for 5 h, a red precipitate was collected by filtration, washed with ethanol, and dried under vacuum. Red crystals suitable for X-ray diffraction were obtained from evaporation of a solution of **L**₁ in dichloromethane and ethanol; yield 65%. IR (KBr): $\tilde{v} = 2916$, 1623, 1598, 1551, 1457, 1411, 1242, 988, 886, 819, 772, 586, 502 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 8.86 (d, *J* = 5.0 Hz, 2 H), 8.54 (s, 1 H), 7.84 (d, *J* = 5.5 Hz, 2 H), 7.37 (s, 1 H), 7.35 (s, 1 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 2.53 (s, 6 H) ppm. MS (MALDI-TOF): m/z = 449.9 [M]⁺. C₁₈H₁₄N₂S₆ (450.71): calcd. C 47.97, H 3.13, N 6.21; found C 48.02, H 3.10, N 6.27.

L_a-Imine-3-pyridyl (L₂): L₂ was obtained from **L**_a and pyridine-3carbaldehyde according to a similar procedure to that described above for **L**₁.Red crystals suitable for X-ray diffraction were obtained from evaporation of a solution of **L**₂ in chloroform; yield 62%. IR (KBr): $\tilde{v} = 2919$, 1615, 1454, 1417, 1324, 1203, 1125, 1024, 891, 810, 772, 706, 467 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): $\delta =$ 9.01 (s, 1 H), 8.72 (d, J = 4.5 Hz, 1 H), 8.50 (s, 1 H), 8.30 (d, J =8.0 Hz, 1 H), 7.45 (dd, J = 8.0, 5.0 Hz, 1 H), 7.27 (s, 1 H), 7.16 (d, J = 1.0 Hz, 1 H), 7.03 (d, J = 8.0 Hz, 1 H), 2.44 (s, 6 H) ppm. MS (MALDI-TOF): m/z = 450.1 [M]⁺. C₁₈H₁₄N₂S₆ (450.71): calcd. C 47.97, H 3.13, N 6.21; found C 48.02, H 3.10, N 6.27.

L_b-Imine-2-pyridyl (L₃): L₃ was obtained according to a similar procedure to that described above for L₁ starting from L_b and pyridine-2-carbaldehyde; yield 59%. IR (KBr): $\tilde{v} = 2911$, 1626, 1584, 1562, 1466, 1408, 1259, 1113, 996, 876, 805, 773, 740, 584, 893 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.76$ (d, J = 3.5 Hz, 1 H), 8.63 (s, 1 H), 8.21 (d, J = 8.0 Hz, 1 H), 7.87 (t, 1 H), 7.43 (q, 1 H), 7.31 (s, 2 H), 7.13 (d, J = 8.0 Hz, 1 H), 3.35 (s, 4 H) ppm. MS (MALDI-TOF): m/z = 448.1 [M]⁺. C₁₈H₁₂N₂S₆ (448.69): calcd. C 48.18, H 2.69, N 6.24; found C 48.14, H 2.63, N 6.27.

[Cu(hfac)₂(L₁)₂] (4): A solution of L₁ (9.0 mg, 0.02 mmol) in dichloromethane (5 mL) was added to a hot solution of Cu(hfac)₂·2H₂O (10.4 mg, 0.02 mmol) in hexane (6 mL). The dark red mixture was stirred at room temperature for 15 min. Slow evaporation of the resulting solution in the dark gave wine-colored platelets of 4, which were suitable for single-crystal X-ray diffraction; yield 70%. IR (KBr): $\tilde{v} = 2924$, 1642, 1615, 1555, 1525, 1482, 1427, 1322, 1258, 1202, 1140, 1030, 870, 825, 790, 773, 688, 668, 587 cm⁻¹.

 $[Mn(hfac)_2(L_1)_2]$ (5): Dark red crystals 5 were obtained according to a similar procedure to that described for 4 with Mn(hfac)_2·2H₂O instead of Cu(hfac)_2·2H₂O; yield 81%. IR (KBr): $\tilde{v} = 2906, 2359,$ 1645, 1610, 1555, 1522, 1490, 1455, 1421, 1323, 1254, 1191, 1142, 1012, 969, 884, 823, 789, 771, 687, 663, 583 cm⁻¹.

 $[Cu(hfac)_2(L_2)_2]$ (6): Dark red crystals 6 were obtained according to a similar procedure to that described for 4 with L_2 instead of L_1 ; yield 63%. IR (KBr): $\tilde{v} = 2920$, 1645, 1616, 1557, 1531, 1463, 1422, 1344, 1258, 1208, 1138, 1087, 868, 824, 800, 774, 744, 669, 582 cm⁻¹.

[Re(CO)₄(L₃)][Re₂(CO)₆Cl₃] (7): Under a nitrogen atmosphere, a mixture of Re(CO)₅Cl (37 mg, 0.1 mmol) and L₃ (49 mg, 0.1 mmol) in toluene (8 mL) was heated to reflux for 2 h to give a black suspension, which was cooled to room temperature, and the resulting precipitate was collected by filtration. The crude solid was purified by flash chromatography using dichloromethane as the eluent; yield 84%. Black crystals were obtained by diffusing diethyl ether into a dichloromethane solution of 7. IR (KBr): $\tilde{v} = 2020$, 1959, 1927, 1886, 1474, 1453, 1355, 1302, 1236, 1114, 809, 770, 643, 530 cm⁻¹. ¹H NMR (500 MHz, DMSO): $\delta = 9.34$ (s, 1 H), 9.06 (d, J = 5.5 Hz, 1 H), 8.35 (t, 2 H), 7.85 (m, 1 H), 7.74 (d, J = 8.5 Hz, 1 H), 7.72 (d, J = 2.0 Hz, 1 H), 7.44 (dd, J = 8.5, 6.5 Hz, 1 H), 3.40 (s, 4 H) ppm. ESI-MS: m/z = 747.00 [Re(CO)₄(L₃)]⁺, 646.92 [Re₂(CO)₆-Cl₃]⁻, 341.33 [Re (CO)₃Cl₂]⁻.

Crystal Structure Determination: The data were collected with a Bruker Smart Apex CCD diffractometer equipped with graphite monochromated Mo- K_a radiation ($\lambda = 0.71073$ Å) using a ω -2 θ

scan mode at 293 K. The highly redundant data sets were reduced with SAINT^[42] and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS^[43] supplied by Bruker. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXTL-97.^[44] All non-hydrogen atoms were found by alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of U_{iso} .

CCDC-831433 (for L_a), -831434 (for L_b), -831435 (for L_1), -831436 (for L_2), -831437 (for 4), -831438 (for 5), -831439 (for 6), and -831440 (for 7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected bond lengths and angles of the ligands, the structures of L_a and L_b .

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