



New Re(I) tricarbonyl-diimine complexes with *N,N'*-bis(substituted benzaldehyde)-1,2-diiminoethane Schiff base ligands: Synthesis, spectroscopic and electrochemical studies and crystal structures

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ABSTRACT

The syntheses, structures and spectroscopic properties of tricarbonylrhenium(I) complexes with *N,N'*-bis(2-bromo, 4-bromo, 4-chloro and 3-methoxybenzaldehyde)-1,2-diiminoethane Schiff base ligands have been investigated in this paper. Characterization of these complexes was carried out with FTIR, NMR, UV–Vis spectroscopy, elemental analysis and X-ray crystallography. The electrochemical behavior of the investigated complexes has been studied by cyclic voltammetry. The crystal structures of the 4-chloro, 4-bromo and 4-methoxy substituted complexes are stabilized by intermolecular C–H···Cl and C–H···O hydrogen bonds. The remarkable features of the 2-bromo, 4-bromo and 4-chloro substituted complexes are short intermolecular halogen–oxygen contacts. In the 4-bromo complex, short intermolecular Br···O and O···O contacts link neighboring molecules along the [1 0 0] direction, which are further stabilized by short intermolecular π ··· π interactions. In 2-bromo complex, intermolecular Br···O interactions link neighboring molecules into 1D extended chains along the [0 1 0] and [0 0 1] directions, forming a 2D network which is parallel to the *bc*-plane.

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1. Introduction

The *fac*-[Re(CO)₃(L)X]^{0/+} complexes, where L is a bi-functional Schiff base ligand and X is a halogen atom or another ligand approximately axial to the aromatic rings plane, have aroused recent attention [1,2]. Their ease of synthesis, multi-denticity, combination of donor atoms and stability have made Schiff bases the preferred ligand system for use as radiopharmaceuticals [3], in catalysis [4] and as model systems for biological macromolecules [5].

Unique photophysical and physicochemical properties of Re(I) tricarbonyl-diimine complexes are connected with the existence of energetically low-lying charge transfer excited states with large electron density shift from the metal to the diimine ligand (MLCT state). Because of the powerful reductive and/or oxidative properties in the MLCT state, such complexes can be considered as photosensitizer, e.g., in photovoltaic cells [6,7]. Their photochemical properties have been utilized for the electrocatalytic and photocatalytic reduction [8,9] of CO₂ to CO. Several tricarbonylrhenium(I) complexes have been used as electroluminescent materials in OLED-type devices [10,11]. Rhenium carbonyl-diimine complexes

are, depending on their structure and environment, promising sensitizers, luminophores, photocatalysts, radical photoinitiators and luminescent probes or sensors. Their potential function depends on the character and properties of their lowest excited state, and hence control of the excited state resulting from a MLCT transition and the redox properties of the [Re(CO)₃(L)X] complexes through structural and electronic modification in the axial or diimine ligands can be a way of improving the photo- and electro-catalytic properties of these compounds.

In this work, we report the synthesis, characterization, electrochemistry and the crystal structures of [Re(CO)₃(4-cbzen)Cl] (**1**), [Re(CO)₃(4-bbzen)Cl] (**2**), [Re(CO)₃(2-bbzen)Cl] (**3**) and [Re(CO)₃(3-mbzen)Cl] (**4**), in which 4-cbzen = *N,N'*-bis(4-chlorobenzaldehyde)-1,2-diiminoethane, 4-bbzen = *N,N'*-bis(4-bromobenzaldehyde)-1,2-diiminoethane, 2-bbzen = *N,N'*-bis(2-bromobenzaldehyde)-1,2-diiminoethane and 3-mbzen = *N,N'*-bis(3-methoxybenzaldehyde)-1,2-diiminoethane.

2. Experimental

2.1. General

All chemicals were of reagent grade and were used without further purification. The solvents were dried before use with the appropriate drying reagents.

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Table 1
Crystal data and structure refinement parameters for complexes 1–4.

Complex	1	2	3	4
Formula	C ₁₉ H ₁₄ Cl ₃ N ₂ O ₃ Re	C ₁₉ H ₁₄ Br ₂ ClN ₂ O ₃ Re	C ₁₉ H ₁₄ Br ₂ ClN ₂ O ₃ Re	C ₂₁ H ₂₀ ClN ₂ O ₃ Re
Formula weight	610.87	699.79	699.79	602.04
Crystal size (mm)	0.34 × 0.19 × 0.17	0.70 × 0.21 × 0.11	0.41 × 0.40 × 0.29	0.21 × 0.15 × 0.14
Colour	colourless	colourless	colourless	pale-yellow
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>n</i>
θ_{\max} (°)	32.5	37.5	40	32.3
<i>a</i> (Å)	7.1111(1)	7.1532(8)	16.3744(3)	13.7332(3)
<i>b</i> (Å)	10.0136(1)	10.2750(12)	9.7068(2)	10.6295(2)
<i>c</i> (Å)	14.6812(1)	14.7417(17)	13.8832(3)	14.6455(2)
α (°)	73.50(1)	73.097(6)	90	90
β (°)	83.72(1)	84.124(6)	111.288(1)	93.380(1)
γ (°)	77.58(2)	77.064(6)	90	90
<i>V</i> (Å ³)	977.598(18)	1009.6(2)	2056.07(7)	2134.19(7)
<i>Z</i>	2	2	4	4
<i>D</i> _{calc} (Mg/m ³)	2.075	2.302	2.261	1.874
μ (mm ⁻¹)	6.65	10.13	9.95	5.85
<i>F</i> (0 0 0)	584	656	1312	1168
Index ranges	−10 ≤ <i>h</i> ≤ 10 −15 ≤ <i>k</i> ≤ 15 −22 ≤ <i>l</i> ≤ 21	−12 ≤ <i>h</i> ≤ 12 −17 ≤ <i>k</i> ≤ 17 −25 ≤ <i>l</i> ≤ 25	−28 ≤ <i>h</i> ≤ 28 −17 ≤ <i>k</i> ≤ 17 −24 ≤ <i>l</i> ≤ 25	−17 ≤ <i>h</i> ≤ 20 −14 ≤ <i>k</i> ≤ 15 −21 ≤ <i>l</i> ≤ 21
Number of measured reflections	37 585	47 946	85 299	31 765
Number of independent reflections (<i>R</i> _{int})	6699/0.026	10 572/0.042	12 645/0.049	7510/0.055
Number of observed reflections [<i>I</i> > 2σ(<i>I</i>)]	6675	9294	10 524	5241
Number of parameters	253	253	253	273
Goodness-of-fit (GOF) on <i>F</i> ²	1.03	1.05	1.04	0.97
<i>R</i> ₁ (observed data)	0.016	0.0308	0.0403	0.0374
<i>wR</i> ₂ (all data) ^a	0.0348	0.0766	0.1083	0.0789

^a $w = 1/[\sigma^2(F_o^2) + (0.0127P)^2 + 0.7305P]$ for 1, $w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.7477P]$ for 2, $w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.8024P]$ for 3 and $w = 1/[\sigma^2(F_o^2) + (0.0351P)^2]$ for 4, where $P = (F_o^2 + 2F_c^2)/3$.

Elemental analyses were performed on a Leco, CHNS-932 analyzer. IR spectra were recorded on an IRPrestige-21 Shimadzu FTIR instrument in KBr pellets. NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer. Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer. Emission spectra were recorded on a RF-5000 Shimadzu spectrofluorophotometer at room temperature from solution samples in CH₂Cl₂. Cyclic voltammetry (CV) was done using a three-electrode cell containing Ag/AgNO₃ in CH₃CN reference electrode, a Pt wire counter electrode and a glassy carbon (GC) working electrode. These measurements were performed in CH₂Cl₂ containing 0.02 M Bu₄NClO₄ (TBAP) as a supporting electrolyte.

2.2. Crystal structure determination

Single crystals of [Re(CO)₃(4-cbzen)Cl] (**1**), [Re(CO)₃(4-bbzen)Cl] (**2**), [Re(CO)₃(2-bbzen)Cl] (**3**) and [Re(CO)₃(3-mbzen)Cl] (**4**), suitable for X-ray diffraction analysis, were grown by slow evaporation of a solution of complexes dissolved in CH₂Cl₂ and toluene (2:1). The crystallographic data and refinement parameters of the complexes are listed in Table 1. Data were collected on a Bruker SMART APEXII CCD area detector diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) equipped with an Oxford cryo-system Cobra low temperature attachment. Cell parameters were retrieved using SMART [12] software and refined using SAINT [13] on all observed reflections. Data reduction and correction for Lp (Lorentz-polarization) and decay were performed using SAINT PLUS software. Absorption corrections were applied using SADABS [14]. The structure was solved by direct methods and refined by the least squares method on *F*² using the SHELXTL program package [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined with a riding model approximation with their parameters constrained to the parent atom with *U*_{iso} (H) = 1.2 or 1.5 *U*_{eq} (C).

2.3. Synthesis of the ligands

2.3.1. *N,N'*-Bis(4-chlorobenzaldehyde)-1,2-diiminoethane (4-cbzen)

In a 50 mL round-bottomed flask, 3 mmol (0.2 mL) of ethylenediamine was added to a CH₂Cl₂ solution of 6 mmol of 4-chlorobenzaldehyde (0.84 g). After stirring at room temperature for 3 h, the solution was filtered and the resulting solid was recrystallized from ethanol. FTIR (KBr, cm⁻¹): ν_{\max} 1643 (C=N). ¹H NMR (*d*⁶-DMSO, δ_{ppm}): 4.00 (s, 4H, -CH₂-CH₂-); 7.39–7.67 (m, 8H, aromatic hydrogens); 8.27 (s, 2H, iminic hydrogens).

2.3.2. *N,N'*-Bis(4-bromobenzaldehyde)-1,2-diiminoethane (4-bbzen)

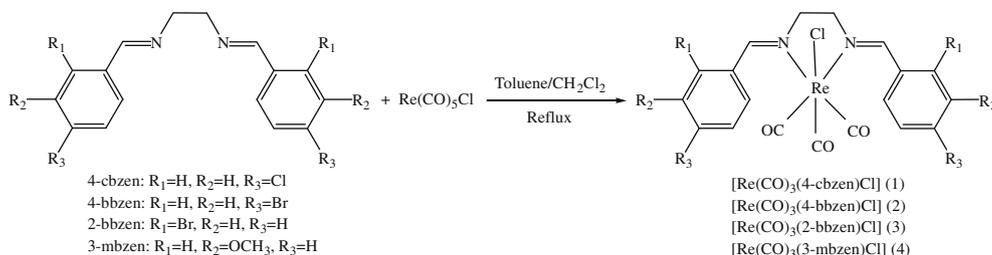
This ligand was prepared by a procedure similar to 4-cbzen ligand, but using 4-bromobenzaldehyde (1.11 g). The solid was collected by filtration and recrystallized from ethanol. FTIR (KBr, cm⁻¹): ν_{\max} 1643 (C=N). ¹H NMR (*d*⁶-DMSO, δ_{ppm}): 3.88 (s, 4H, -CH₂-CH₂-); 7.62–7.67 (m, 8H, aromatic hydrogens); 8.33 (s, 2H, iminic hydrogens).

2.3.3. *N,N'*-Bis(2-bromobenzaldehyde)-1,2-diiminoethane (2-bbzen)

This ligand was prepared by a procedure similar to that for 4-cbzen ligand, except that 0.7 mL of 2-bromobenzaldehyde was used. The solution was filtered and the resulting solid was recrystallized from ethanol. FTIR (KBr, cm⁻¹): ν_{\max} 1632 (C=N). ¹H NMR (*d*⁶-DMSO, δ_{ppm}): 3.96 (s, 4H, -CH₂-CH₂-); 7.36–7.94 (m, 8H, aromatic hydrogens); 8.56 (s, 2H, iminic hydrogens).

2.3.4. *N,N'*-Bis(3-methoxybenzaldehyde)-1,2-diiminoethane (3-mbzen)

This ligand was prepared by a procedure similar to that for 4-cbzen ligand, except that 0.73 mL of 3-methoxybenzaldehyde was used. The solution was filtered and the resulting solid was recrystallized from ethanol. FTIR (KBr, cm⁻¹): ν_{\max} 1645 (C=N). ¹H NMR (*d*⁶-DMSO, δ_{ppm}): 3.76 (s, 6H, methoxy hydrogens), 3.88



Scheme 1. Preparation of the characterized Re(I) tricarbonyl-diimine complexes.

Table 2

UV–Vis spectral data of the ligands and complexes **1–4** in CH₂Cl₂ (4×10^{-5} M).

Compound	λ_{\max} (nm) [ϵ] (M ⁻¹ cm ⁻¹)
4-cbzen	245 [26 750], 290 [9500]
4-bbzen	252 [39 450], 292 [5000]
2-bbzen	250 [27 720], 291 [3275]
3-mbzen ^a	245 [14 333], 300 [6500]
Complex 1	235 [15 025], 261 [32 500], 373 [1825] ^b
Complex 2	233 [12 750], 261 [28 750], 370 [1800] ^b
Complex 3	233 [13 250], 257 [17 950], 366 [1712] ^b
Complex 4	238 [19 833], 258 [21 966], 369[1770] ^b

^a $C = 12 \times 10^{-5}$ M

^b $C = 1 \times 10^{-3}$

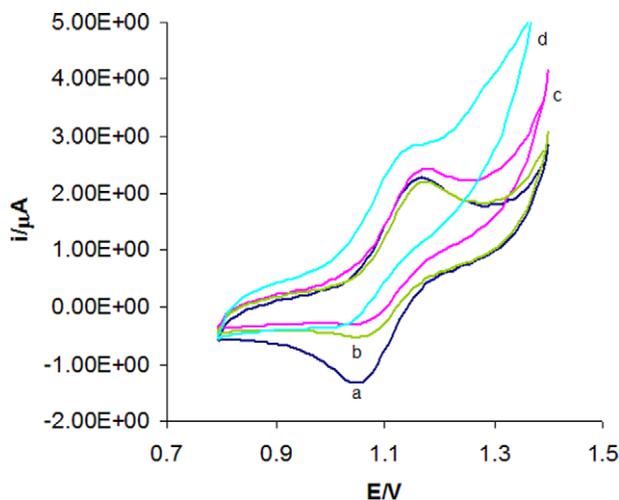


Fig. 1. Cyclic voltammograms of [Re(CO)₃(2-bbzen)Cl] (a), [Re(CO)₃(4-cbzen)Cl] (b), [Re(CO)₃(4-bbzen)Cl] (c) and [Re(CO)₃(3-mbzen)Cl] (d) in CH₂Cl₂ at 298 K (scan rate = 100 mV/s, $C = 2 \times 10^{-4}$ M).

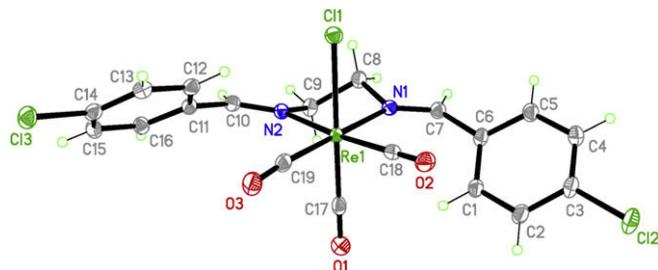


Fig. 2. The molecular structure of complex **1**, showing 50% probability displacement ellipsoids and the atomic numbering.

(s, 4H, $-\text{CH}_2-\text{CH}_2-$); 6.96–7.44 (m, 8H, aromatic hydrogens); 8.31 (s, 2H, iminic hydrogens).

2.4. Synthesis of the rhenium complexes

2.4.1. [Re(CO)₃(4-cbzen)Cl] (**1**)

To a 50 mL round-bottom flask containing 0.55 mmol (0.17 g) of 4-cbzen dissolved in 20 mL of degassed CH₂Cl₂ and toluene (1:2), was added an equimolar amount of Re(CO)₅Cl (0.2 g). The mixture was heated at reflux for 4 h. The solution was concentrated to half volume and *n*-hexane was added to precipitate the complex. *Anal.* Calc. for C₁₉H₁₄ClN₄O₇Re: C, 37.36; H, 2.29; N, 4.58. Found: C, 37.29; H, 2.34; N, 4.51%. FTIR (KBr, cm⁻¹): ν_{\max} 2021, 1916 and 1889 (CO); 1626 (C=N). ¹H NMR (*d*⁶-DMSO, δ_{ppm}): 4.09–4.13 and 4.23–4.25 (two sets of multiples, 4H, $-\text{CH}_2-\text{CH}_2-$); 7.62–7.89 (m, 8H, aromatic hydrogens); 9.19 (s, 2H, iminic hydrogens). ¹³C{¹H} NMR (*d*⁶-DMSO, δ_{ppm}): 65.42 ($-\text{CH}_2-\text{CH}_2-$); 129.56, 131.52, 135.29, 136.81 (aromatic carbons); 174.22 (iminic carbons); 192.47 (CO); 195.60 (2CO).

2.4.2. [Re(CO)₃(4-bbzen)Cl] (**2**)

This complex was synthesized by a procedure similar to **1**, but using the 4-bbzen ligand (0.22 g). *Anal.* Calc. for C₁₉H₁₄ClN₄O₇Re: C, 32.62; H, 2.00; N, 4.00. Found: C, 32.53; H, 1.97; N, 3.99%. FTIR (KBr, cm⁻¹): ν_{\max} 2019, 1913 and 1886 (CO); 1630 (C=N). ¹H NMR (*d*⁶-DMSO, δ_{ppm}): 4.09–4.12 and 4.22–4.25 (two sets of multiples, 4H, $-\text{CH}_2-\text{CH}_2-$); 7.76–7.81, (m, 8H, aromatic hydrogens); 9.17 (s, 2H, iminic hydrogens). ¹³C{¹H} NMR (*d*⁶-DMSO, δ_{ppm}): 65.42 ($-\text{CH}_2-\text{CH}_2-$); 125.96, 131.63, 132.47, 135.64 (aromatic carbons); 174.31 (iminic carbons); 192.46 (CO); 195.6 (2CO).

2.4.3. [Re(CO)₃(2-bbzen)Cl] (**3**)

This complex was prepared by a procedure similar to that for **1**, but using the 2-bbzen ligand (0.22 g). *Anal.* Calc. for C₁₉H₁₄ClN₄O₇Re: C, 32.62; H, 2.00; N, 4.00. Found: C, 32.45; H, 1.86; N, 3.95%. FTIR (KBr, cm⁻¹): ν_{\max} 1900 (broad) and 2017 (CO); 1625 (C=N). ¹H NMR (*d*⁶-DMSO, δ_{ppm}): 4.15–4.19 and 4.38–4.42 (two sets of multiples, 4H, $-\text{CH}_2-\text{CH}_2-$); 7.45–7.79 (8H, aromatic hydrogens); 9.16 (s, 2H, iminic hydrogens). ¹³C{¹H} NMR (*d*⁶-DMSO, δ_{ppm}): 64.38 ($-\text{CH}_2-\text{CH}_2-$); 121.67, 128.63, 131.58, 133.07, 133.27, 137.59 (aromatic carbons); 173.94 (iminic carbons); 192.17 (CO); 194.93 (2CO).

2.4.4. [Re(CO)₃(3-mbzen)Cl] (**4**)

This complex was prepared by a procedure similar to that for **1**, but using the 3-mbzen ligand (0.16 g). *Anal.* Calc. for C₁₉H₁₄ClN₄O₇Re: C, 41.91; H, 3.32; N, 4.65. Found: C, 41.25; H, 3.36; N, 4.65%. FTIR (KBr, cm⁻¹): ν_{\max} 2019, 1921 and 1889 (CO); 1630 (C=N). ¹H NMR (*d*⁶-DMSO, δ_{ppm}): 3.82 (s, 6H, methoxy hydrogens), 4.11–4.13 and 4.23–4.25 (two sets of multiples, 4H, $-\text{CH}_2-\text{CH}_2-$); 7.10–7.62 (m, 8H, aromatic hydrogens); 9.18 (s, 2H, iminic hydrogens). ¹³C{¹H} NMR (*d*⁶-DMSO, δ_{ppm}): 65.5 ($-\text{CH}_2-\text{CH}_2-$); 114.51, 118.37, 122.09, 130.69, 137.47, 159.97 (aromatic carbons); 174.76 (iminic carbons); 192.8 (CO); 195.68 (2CO).

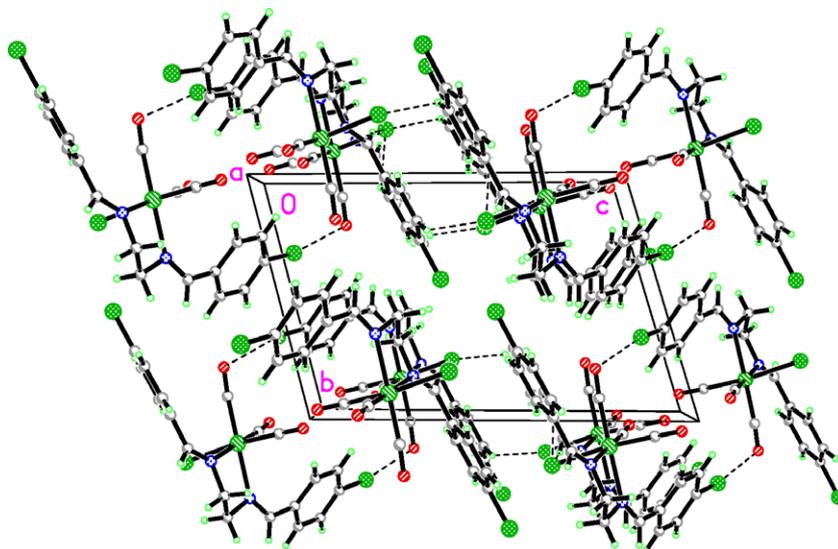


Fig. 3. The crystal packing of complex 1, viewed down the *a*-axis showing intermolecular Cl...O interactions.

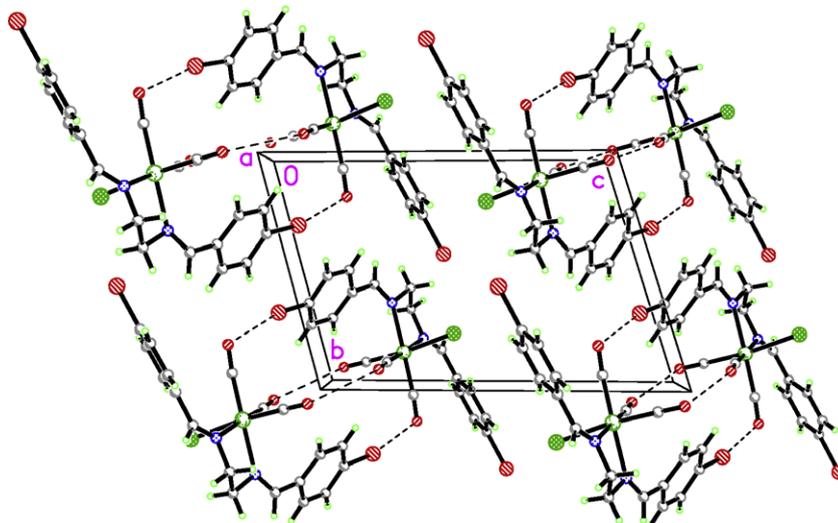


Fig. 4. The crystal packing of complex 2, viewed down the *a*-axis showing intermolecular Br...O interactions.

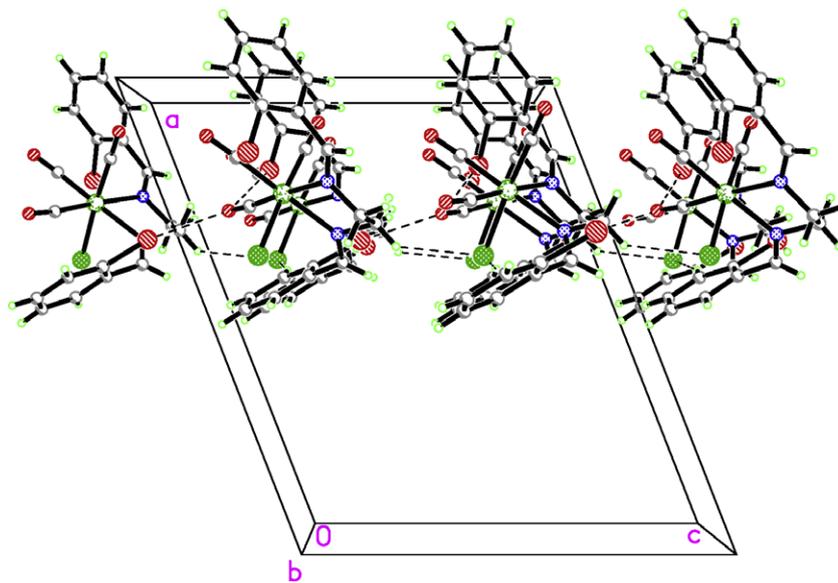


Fig. 5. The crystal packing of complex 3, viewed down the *b*-axis showing short intermolecular Br...O contacts, forming 1D extended chains along the *c*-axis.

3. Results and discussion

3.1. General characterization

The synthetic routes of complexes **1–4** are outlined in Scheme 1. The new complexes are stable in the solid and solution states, and they were characterized by the usual spectroscopic techniques.

The IR spectra of the complexes show three or two (one peak is broad) strong bands in the carbonyl region ($1880\text{--}2010\text{ cm}^{-1}$) which arise from a facial conformation around a hexa-coordinated rhenium. The π -donor character of the chlorine atom increases the Re–CO back-bonding, which decreases the energy of $\nu(\text{CO})$. Coordination of the diimine ligands are indicated by the shifts of $\nu(\text{C}=\text{N})$ from 1643 cm^{-1} in the free ligand to 1626 cm^{-1} in **1**, from 1643 to 1620 cm^{-1} in **2**, from 1632 to 1625 cm^{-1} in **3** and from 1645 to 1630 cm^{-1} in **4**.

In the ^1H NMR spectra of complexes **1–4**, which are presented in the experimental section, the signals are shifted to the low-field region with respect to the free ligands, as a result of ligand coordination. The chemical shifts observed at δ 9.19 for **1**, at δ 9.17 for **2**, at δ 9.16 for **3** and at δ 9.18 for **4** are assigned to the proton of azomethine ($-\text{CH}=\text{N}-$) as a singlet. The signals of the $-\text{CH}_2-\text{CH}_2-$ protons appear as two sets of multiples in the complexes, but appeared as a singlet (at 3.76–4 ppm) in the free ligands, indicating that the methylene protons of the complexes are magnetically non-equivalent. The ^{13}C NMR spectra of the complexes show two signals with an integral of 2:1 in the range 192–196 ppm, and the downfield peaks are ascribed to the two carbonyl groups *cis* to the chloride while the upfield resonance is assigned to the carbonyl *trans* to the chloride.

The UV–Vis spectroscopic data for the ligands and complexes are given in Table 2. The bands of the diimine ligands are due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [16]. In general, the electronic absorption spectra of rhenium(I) diimine complexes show intense high-energy absorption bands at ca. 230–330 nm and low-energy absorption bands at ca. 400 nm [17,18]. The former, which are also found in the free ligands, are assigned as $\pi \rightarrow \pi^*$ transitions and the later are tentatively assigned as $d\pi(\text{Re}) \rightarrow \pi^*$ (diimine) metal-to-ligand charge transfer (MLCT) transitions. The spectral positions of the $\pi \rightarrow \pi^*$ bands in the complexes are red-shifted in comparison to the ligand, due to the coordination of the heavy metal core. The complexes **1–4** do not show emission in CH_2Cl_2 at room temperature. Fig. 1 shows cyclic voltammograms of the complexes in CH_2Cl_2 under a nitrogen atmosphere. Complexes **1–4** show a quasi-reversible Re(I/II) redox couple with $E_{1/2}$ values of 1.11, 1.12, 1.11 and 1.12 V versus Ag/AgNO₃ (in CH_3CN), respectively. In the cyclic voltammogram, peak to peak separations (ΔE_p) of 90, 90, 100 and 160 mV were observed at a scan rate (v) of 100 mV/s for complexes **1–4**, respectively.

3.2. Structural characterization

The perspective drawing of complex **1** and the crystal packing of complexes **1–4** are shown in Figs. 2–6. In general, the coordination geometries of the prepared complexes are distorted octahedral, due to the chelating effect of the rigid diimine ligands. The three terminal CO ligands coordinated with the Re are arranged in a facial fashion, which is similar to those found in other related rhenium systems [19–21]. Selected bond lengths and bond angles of the complexes are presented in Table 3. The Re–N bond lengths in these complexes are in the range of reported for other previously synthesized complexes [22,23]. Due to the π -donor character of the chloride ligand, the length of the axial Re–C bonds is slightly shorter than the values of the equatorial Re–C bonds. The diimine ligands bite angles of $78.52(5)^\circ$ for **1**, $78.15(8)^\circ$ for **2**, $77.35(8)^\circ$ for **3**

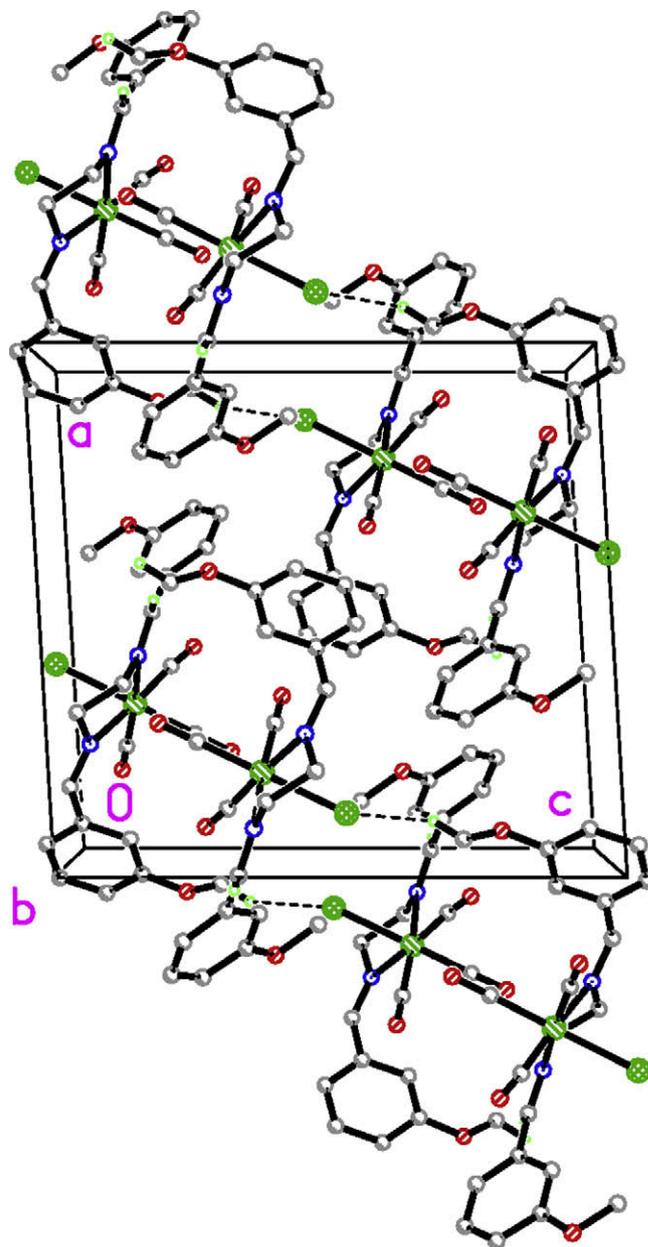


Fig. 6. The crystal packing of complex **4**, viewed down the *b*-axis showing linking of molecules by intermolecular interactions. Only the H atoms involved the interaction are shown.

and $77.73(11)^\circ$ for **4** slightly deviate from the expected ideal 90° for an octahedron. As can be seen in Table 3, the *trans* angles at the Re(I) site are in the range $172.88(6)\text{--}176.23(9)^\circ$, showing a slight deviation from an ideal octahedral arrangement. Hydrogen bonding interactions in complexes **1**, **2** and **4**, $\text{C}-\text{H}\cdots\text{X}$ ($\text{X} = \text{O}$ and Cl), are listed in Table 4, which stabilize the crystal structures. Complex **3** does not show any classic hydrogen bonds. The interesting features of complexes **1**, **2** and **3** are the short intermolecular $\text{Cl}\cdots\text{O}$, $\text{Br}\cdots\text{O}$, $\text{O}\cdots\text{O}$, and $\text{Br}\cdots\text{O}$ contacts, respectively, which are listed in Table 5. In complex **1**, the short intermolecular $\text{Cl}\cdots\text{O}$ contacts link neighboring molecules into individual dimers which are further connected by $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds (Fig. 3). In complex **2**, the short intermolecular $\text{Br}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ contacts link neighboring molecules into a chain along the $[100]$ direction (Fig. 4). These contacts are shorter than the sum of the van der Waals radii of these atoms. Complex **2** is further stabilized by intermolecular

Table 3
Selected bond distances (Å) and angles (°).

Complex 1			
Re(1)–Cl(1)	2.4886(4)	N(1)–Re(1)–N(2)	78.52(5)
Re(1)–N(1)	2.2237(16)	N(1)–Re–C(18)	98.36(7)
Re(1)–N(2)	2.1859(14)	N(2)–Re–C(19)	98.58(6)
Re(1)–C(17)	1.9163(18)	C(17)–Re–C(18)	92.36(7)
Re(1)–C(18)	1.9321(15)	C(17)–Re–C(19)	87.30(8)
Re(1)–C(19)	1.910(2)	C(17)–Re(1)–Cl(1)	172.88(6)
Complex 2			
Re(1)–Cl(1)	2.4929(7)	N(1)–Re(1)–N(2)	78.15(8)
Re(1)–N(1)	2.188(2)	N(1)–Re–C(17)	98.62(10)
Re(1)–N(2)	2.225(2)	N(2)–Re–C(19)	98.14(11)
Re(1)–C(17)	1.913(3)	C(18)–Re–C(17)	86.46(12)
Re(1)–C(18)	1.918(3)	C(18)–Re–C(19)	92.08(11)
Re(1)–C(19)	1.937(3)	C(18)–Re(1)–Cl(1)	173.53(9)
Complex 3			
Re(1)–Cl(1)	2.4884(7)	N(1)–Re(1)–N(2)	77.35(8)
Re(1)–N(1)	2.186(3)	N(1)–Re–C(18)	98.82(10)
Re(1)–N(2)	2.193(2)	N(2)–Re–C(17)	98.39(10)
Re(1)–C(17)	1.921(3)	C(19)–Re–C(17)	90.02(12)
Re(1)–C(18)	1.911(3)	C(19)–Re–C(18)	86.48(12)
Re(1)–C(19)	1.909(3)	C(19)–Re(1)–Cl(1)	176.23(9)
Complex 4			
Re(1)–Cl(1)	2.4835(10)	N(1)–Re(1)–N(2)	77.73(11)
Re(1)–N(1)	2.195(3)	N(1)–Re–C(19)	99.48(15)
Re(1)–N(2)	2.199(3)	N(2)–Re–C(21)	97.17(15)
Re(1)–C(19)	1.912(4)	C(20)–Re–C(19)	86.58(18)
Re(1)–C(20)	1.913(4)	C(20)–Re–C(21)	90.87(18)
Re(1)–C(21)	1.929(4)	C(20)–Re(1)–Cl(1)	175.83(13)

Table 4
Parameters of hydrogen bonding interactions in complexes 1–4.

D–H...A	H...A (Å)	D...A (Å)	D–H...A (°)
Complex 1			
C(10)–H(10A)...Cl(1) ⁱ	2.7300	3.5910(16)	155.00
C(12)–H(12A)...Cl(1)	2.7900	3.6529(18)	155.00
Complex 2			
C(1)–H(1A)...Cl(1)	2.7800	3.654(3)	156.00
C(7)–H(7A)...Cl(1) ⁱ	2.7500	3.616(3)	155.00
Complex 4			
C(5)–H(5A)...Cl(1)	2.6200	3.505(4)	158.00
C(7)–H(7A)...O(5) ⁱⁱ	2.6000	3.426(5)	148.00
C(18)–H(18A)...Cl(1) ⁱⁱⁱ	2.6500	3.526(4)	151.00

Symmetry codes: (i) $1+x, y, z$; (ii) $3/2-x, -1/2+y, -1/2-z$; (iii) $1/2+x, -1/2-y, -1/2+z$.

Table 5
The values of X...El, and El...El (X = halogen, El = electronegative atom) short contacts (Å) in complexes 1–4.

Complex 1	Complex 2	Complex 3
Cl(2)...O(3) 3.1126(16)	Br(1)...Cl(1) 3.6143(9)	Br(1)...O(2) 2.943(2)
	Br(2)...O(1) 3.117(3)	Br(2)...O(2) 3.255(2)
	O(2)...O(3) 3.026(3)	

Symmetry codes: (i) $-x, -y, -z$ (ii) $-1-x, -y, -z$ (iii) $x, 1/2-y, -1/2+z$ (iv) $x, 1+y, z$.

$\pi \cdots \pi$ interactions with centroid to centroid distances of 3.6065(16) and 3.7993(18) Å, [Cg1...Cg1ⁱ and Cg2...Cg2ⁱⁱ, (i) $1-x, -y, -1-z$ and (ii) $-1-x, 1-y, -z$; Cg1 and Cg2 are the centroids of the C1–C6 and C11–C16 benzene rings, respectively]. In complex 3, the short intermolecular Br...O interactions link neighboring molecules into 1D extended chains along both the [0 1 0] and [0 0 1] directions, forming a 2D network which is parallel to the *bc*-plane (Fig. 5). Details of the oxygen–oxygen and halogen–oxygen interactions (X...O) are presented in Table 5.

The attractive nature of these interactions is mainly due to electrostatic effects, but polarization, charge-transfer and dispersion contributions all play an important role [24]. The X...El (X = Halogen, El = Electronegative atom) interactions, or in general non-bonded interactions, are capable of affecting the realized crystalline architecture of solid compounds decisively and they may thus be used as tools in molecular designs, crystal engineering and supramolecular chemistry [25].

4. Conclusion

This work describes the synthesis and characterization of several Re(I)–tricarbonyl complexes with diimine ligands. The ligands were obtained by the condensation of benzaldehyde derivatives with ethylenediamine. All the complexes have been fully characterized by FTIR, ¹H, ¹³C NMR and UV–Vis spectroscopy, elemental analysis and X-ray diffraction analysis. The presence of three strong IR absorptions in the region of CO stretching vibrations is consistent with a facial coordination of the three carbonyl ligands. The molecular units of the complexes are stabilized by intermolecular hydrogen bonds and short intermolecular halogen–oxygen and oxygen–oxygen interactions.

5. Supplementary material

CCDC 694693–694696 contain the supplementary crystallographic data for complexes 1–4, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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