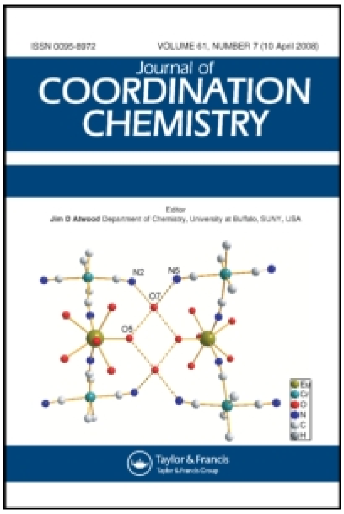

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Tricarbonylrhenium(I) bromide complexes with *N*,*N′*-bis[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine and *N*,*N′*-bis[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine – syntheses, structures, electrochemical and spectroscopic studies

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Two rhenium(I) complexes, $[Re(CO)_3Br(L^n)]$ ($n = 1, 2$), ($L^1 =$ *N*,*N′*-bis[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine and $L^2 =$ *N*,*N′*-bis[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine) have been synthesized and characterized by CHN analyses, ^1H NMR, IR, and UV-Vis spectroscopy. The molecular structure of $[Re(CO)_3Br(L^1)]$ is a distorted octahedron around rhenium with one Br, facial arrangement of three CO's, and one diimine. The UV-Vis spectra of the complexes have metal-to-ligand charge transfer bands increasing in wavelength when the L^2 ligand is replaced by L^1, in agreement with the oxidation potential of the complexes.

Keywords: Bidentate diimine ligand; Electrochemistry; Rhenium complex; X-ray crystallography

1. Introduction

Tricarbonylrhenium(I) complexes *fac*-$Re(CO)_3(L)X$ (L = diimine and X = halide) are of growing interest as these complexes combine ease of preparation, unique photophysical and photochemical properties, and chemical stability [1–7]. Developments are of interest for applications like solar energy conversion, catalytic activity, and use in photoreduction and electroreduction of CO_2 to CO [8–11]. Most studies have been on Re(I) complexes of the type *fac*-$Re(CO)_3(L)X$, where L is 2,2′-bipyridine or 1,10-phenanthroline derivatives. Electronic and steric interactions influence the redox potentials of these complexes, modifying important spectroscopic properties [10–12]. Diimine ligands from acetophenone derivatives to stabilize low valent metal redox-states are good candidates for such studies and were used for the synthesis of Re(I) and

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Cu(I) complexes [13, 14]. Here, we report the synthesis and characterization of Re(I) complexes of the type *fac*-$Re(CO)_3(L)Br$ ($L = N,N'$-bis[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine, **1**, and *N*,*N*′-bis[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine, **2**) with different electronic effects (figure 1). The structure of **1**, spectral properties, and redox chemistry of these complexes are also discussed.

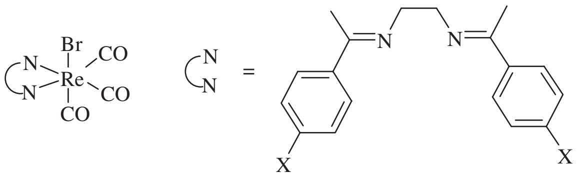
2. Experimental

2.1. *General*

All chemicals were of reagent grade and used as received. Solvents were purified by literature methods [15]. Elemental analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. IR spectra were recorded on a Bruker Tensor 27 instrument. Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer; λ_{max} ($\log \varepsilon$). NMR spectra were obtained on a BRUKER (250 MHz) spectrometer. Proton chemical shifts are reported in parts per million (ppm) relative to an internal standard of Me_4Si. All voltammograms were recorded with a three electrode system consisting of an Ag/AgCl reference electrode, a platinum wire counter electrode, and Au as a working electrode. A Metrohm multipurpose instrument model 693 VA processor with 694A VA stand was used. In all electrochemical experiments the test solution was purged with argon for at least 5 min. L^1 and L^2 were prepared according to reported procedures [14].

2.2. *Syntheses of the complexes*

2.2.1. Synthesis of $Re(L^1)(CO)_3Br$ (1). A mixture of $[Re(CO)_5Br]$ (406 mg, 1 mmol) and L^1 (333 mg, 1 mmol) in dry, degassed toluene (30 cm^3) was heated to reflux for 4 h under N_2 to give a bright red solution. The solvent was removed under vacuum and the crude material recrystallized from CH_2Cl_2/hexane to give $Re(L^1)(CO)_3Br$ as pure red crystals. Yield: 88%. IR (ν, cm^{-1}): 2019, 1914, 1893 (C=O); 1595 ν(C=N). ^{1}H-NMR



Complex	Ligand	X
1	L^1	Cl
2	L^2	NO_2

Figure 1. Chemical formula of **1** and **2**.

(250 MHz, $CDCl_3$): 2.51 (s, 6H, 2-CH_3); 3.99 (dd, 4H, –CH_2CH_2–); 7.53 (m, 8H, Ar-H). λ_{max} (log ε): 311(3.48), 298(4.28), 241(4.24). For $C_{21}H_{18}BrCl_2N_2O_3Re$ Anal. Calcd (%): C 36.91, H 2.65, N 4.10. Found (%): C 36.94, H 2.63, N 4.19.

2.2.2. Synthesis of Re(L^2)$(CO)_3$Br (2). This complex was prepared by a procedure similar to **1** using 354 mg (1 mmol) of L^2. Red crystals were collected by filtration and dried *in vacuo*. Yield: 81%. IR (cm^{-1}, KBr): 2024, 1917, 1885 (C=O); 1582 (C=N); 1351 and 1543 ν(N=O). ^{1}H-NMR (250 MHz, $CDCl_3$): 2.55 (s, 6H, 2-CH_3); 4.10 (dd, 4H, –CH_2CH_2–); 7.80 (m, 8H, Ar-H). λ_{max} (log ε): 346(3.49), 301(4.30), 263(4.25). For $C_{21}H_{18}BrN_4O_7Re$ Anal. Calcd (%): C 35.80, H 2.58, N 7.95. Found (%): C 35.85, H 2.59, N 7.92.

2.3. *Crystal structure determination*

The X-ray measurements of single crystals of *fac*-Re$(CO)_3$(L^1)Br were carried out on a Bruker Kappa CCD single crystal diffractometer equipped with a graphite monochromator and a low temperature device (Oxford Cryosystems). Mo-Kα radiation ($k = 0.71073$ Å) at 100 K were used. The collected data were corrected for Lorentz and polarization effects and numerical absorption correction was applied. The structure was solved by direct methods (SHELXS-97 [16]) and refined using full-matrix least-squares procedures (SHELXL-97 [17]). Non-hydrogen atoms were refined anisotropically, whereas hydrogens were placed in calculated positions, and their thermal parameters were refined isotropically. The details of the X-ray measurements and crystal data for the complex are given in table 1.

3. Results and discussion

3.1. *Complexes*

[Re$(CO)_3$Br(L^n)] ($n = 1, 2$) were prepared by the reaction of the appropriate ligand with [Re$(CO)_5$Br] in toluene and precipitated in analytically pure form. All complexes are soluble in THF and chlorinated solvents and insoluble in ether and hexane. These complexes are stable in air in the solid state for 3 weeks.

3.2. *Structure of 1*

A view of **1** along with the atom-numbering scheme is shown in figure 2. The crystallographic data are summarized in table 1 and selected bond distances and angles are given in table 2. the geometry of the rhenium can be best described as distorted octahedral defined by one bromide, three facial carbonyls, and the diimine ligand (L^1).

The molecule is located on the crystallographic twofold symmetry axis and thus one-half of the molecule is the asymmetric unit of the compound. The Br^- and CO trans to it are mutually disordered by axial twofold symmetry, with each group being present at each location with site occupancy of 50%. The steric requirements of the bidentate ligand causes distortion of the octahedral coordination, clearly seen

Table 1. Crystal data and single crystal X-ray diffraction refinement details for **1**.

Formula	$C_{21}H_{18}BrCl_2N_2O_3Re$
Formula weight	683.38
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	26.7160(4)
b	8.4100(5)
c	10.9770(6)
β	113.142(2)
V (A^3), Z	2267.87(19), 4
Calculated density ($g\,cm^{-3}$)	2.002
Absorption coefficient (mm^{-1})	7.381
Goodness-of-fit on F^2	1.154
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0245$, $wR_2 = 0.0536$
R indices (all data)	$R_1 = 0.0253$, $wR_2 = 0.0538$
Largest difference peak and hole ($e\,Å^{-3}$)	0.656 and −0.778

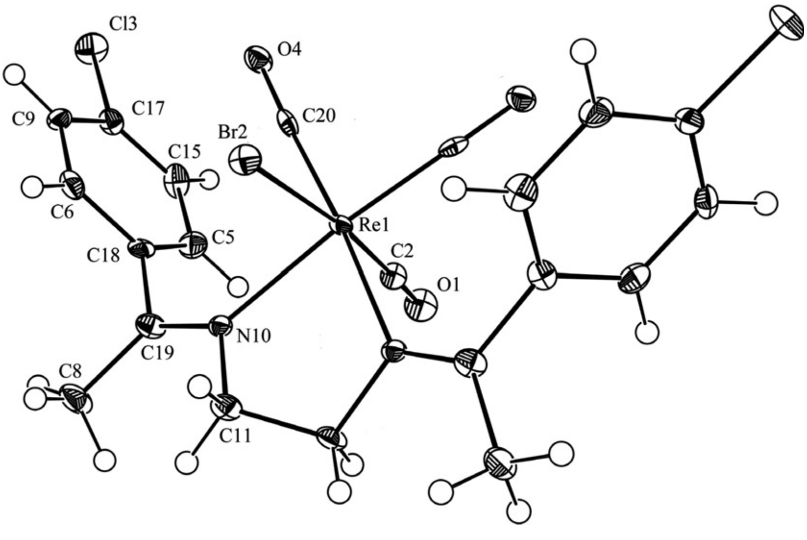


Figure 2. Structure of **1** in the crystal, showing the atom labeling scheme. Thermal ellipsoids with 50% probability.

by bite angles (N(10)–Re(1)–N(10a), 78.4(2)° (table 2). Trans angles at ReI are in the range 173.7(4)–177.8(10)°, also showing a deviation from an ideal octahedral arrangement.

The coordinated bromide is slightly tilted toward L^1, causing a narrowing of the N–Re–Br angles (87.29(16)° for N(10)–Re(1)–Br(2)). The Re–N bond lengths are similar and within the range expected for such complexes [6, 18]. The rhenium–carbonyl bond lengths do not show any significant differences [1.914(6) and 1.921(15) Å] and are

Table 2. Selected bond lengths and angles of **1**.

Re1–C20	1.914(6)	Re1–Br2	2.5605(17)
Re1–N10	2.209(4)	Re1–C2	1.921(15)
C2–O1	1.182(16)	C20–O4	1.158(6)
N10–Re1–N10a	78.4(2)	Br2–Re1–C2	173.7(4)
N10–Re1–Br2	87.29(16)	Br2–Re1–C20	87.29(16)
N10–Re1–C20	174.78(18)	C2–Re1–C20	92.0(4)
N10–Re1–C2	89.9(4)	Re1–C2–O1	177.8(10)
Re1–C20–O4	174.9(4)		

consistent with those observed in similar complexes [6, 19]. The Re–Br bond length, 2.5605(17) Å, is similar to the reported compounds [6].

Despite the fact that the donor nitrogens are sp^2-hybridized, the chelate ring is significantly puckered in this complex, and some strain in the chelate ring is suggested by the deviation from 120° angle about the nitrogen, C(11)–N(10)–Re(1) (109.8(3)°), C(19)–N(10)–Re(1) (132.3(4)°), C(11)–N(10)–C(19) (117.9(4)°). The axis of the complex contains Br2, Re1, C2, and O1 (table 2) and the equatorial plane contains the nitrogens of L^1 and two carbons that are nearly coplanar ($0.5279x + 0.0000y - 0.8493z = -2.7125$). The rhenium is coplanar while two oxygens are displaced to the opposite sides of the plane (O(4) and O(4a) by 0.2202 and −0.2202 Å, respectively). Linking C(11) is 0.34 Å above the N(10)–Re(1)–N(10a) plane while C(11a) is below.

3.3. *IR spectra*

IR spectra show a strong band at $1618\,\mathrm{cm^{-1}}$ for L^1 and $1610\,\mathrm{cm^{-1}}$ for L^2, assigned to the azomethine, ν(C=N) [14, 20]. These bands shift to lower wavenumbers in the complexes, $1595\,\mathrm{cm^{-1}}$ for **1** and $1582\,\mathrm{cm^{-1}}$ for **2**. The observed shift in C=N stretch after complexation confirms the coordination of the azomethine (C=N). The nitro ν(N–O) appears at 1351 and $1543\,\mathrm{cm^{-1}}$ for **2**. The IR spectra for complexes as KBr pellets exhibit three absorptions in the carbonyl stretching region, a sharp intense band at $2019\,\mathrm{cm^{-1}}$, and two closely spaced bands at 1914 and $1893\,\mathrm{cm^{-1}}$ for **1**, about 2024, 1917, and $1885\,\mathrm{cm^{-1}}$ for **2**, typical of the *fac*-Re(I) diimine tricarbonyl complexes [6, 21]. This is consistent with C_s symmetry for the compounds with two A' bands and an A'' band. The wavenumbers of the CO stretches are very sensitive to the d_p electron density of the rhenium center.

3.4. *^{1}H NMR spectra*

Assignments of the complex signals were made by the data reported previously for the free ligands [14]. The methyl protons of the complexes are a singlet at *ca* 2.2 ppm. The A_4 system of the methylene protons for the ligands is converted into an A_2B_2 system when the complexes are formed. On the time scale of the NMR instrument, L^1 and L^2 are conformationally mobile with respect to the C–C bond (methylene carbon) [14], resulting in a singlet for methylene protons. In the complexes the methylene protons are not equivalent because the top side of the molecule (where Br is located) is different from the bottom side (where the axial CO is located), removing the symmetry in the free ligand.

3.5. *Spectroscopic and electrochemical properties*

Absorption spectra of the complexes are quite similar to similar compounds [14]. The electronic spectra have a broad low energy band due to a $d\pi \rightarrow \pi^*$ transition. The absorption spectrum of **1** shows a band at 311 nm. The band of **2** is 35 nm higher in comparison to **1**, indicating enhanced π-accepting of L^2. Additional absorption bands are also observed in the UV region. The intensity of these bands is consistent with intraligand transitions [6, 22].

The electrochemical behavior of the complexes was examined by cyclic voltammetry in CH_3CN and a typical cyclic voltammogram of **1** is indicated in the "Supplementary material." The two ligands are electroinactive in the working potential region. The complexes show an irreversible oxidation wave at 1.33 and 1.23 V (recorded at scan rates $= 0.1\ V\,s^{-1}$) for **1** and **2**, respectively, which can be assigned to a Re^{I}/Re^{II} oxidation [23–25]. The corresponding reduction wave was not observed even under fast scan-rate conditions. The lower redox potential is in accordance with the observed lower wavelength of the first MLCT band of **1** relative to that of **2**.

4. Conclusion

From two chelating ligands, *N*,*N′*-bis[1-(4-chlorophenyl)ethylidene]ethane-1,2-diamine, L^1, and N,N′-bis[1-(4-nitrophenyl)ethylidene]ethane-1,2-diamine, L^2**,** two mononuclear rhenium complexes $[Re(CO)_3Br(L^n)]$ ($n = 1, 2$) (**1**–**2**) have been synthesized. The crystal structure of **1** revealed that the coordination geometry of the rhenium atom can be best described as distorted octahedral geometry defined by one bromide, facial arrangement of three coordinated carbonyls and the diimine ligand (**L**). The position of MLCT is red shifted by 35 nm, when the L^2 ligand is replaced by L^1. A comparison of the $[Re(CO)_3Br(L^n)]$ ($n = 1, 2$) (**1**–**2**) complexes shows a correlation between the spectroscopic and redox properties. Red shift of the MLCT absorption correlates with the decrease of oxidation potential of the complex.

Supplementary material

The crystallographic data for **1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 752156. The copies of these data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033).

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References

[1] L.A. Sacksteder, A.P. Zipp, E.A. Brown, J.J. Streich, N. Demas, B.A. DeGraff. *Inorg. Chem.*, **29**, 4335 (1990).
[2] S.R. Van Wallendael, J.D. Shaver, P.B. Rillema, J. Yoblinski, M. Stathis, T.F. Guarr. *Inorg. Chem.*, **29**, 1761 (1990).
[3] R.D. Sahai, P. Rillema, R. Shaver, S. Van Wallendael, D.C. Jackman, M. Boldaji. *Inorg. Chem.*, **28**, 1022 (1989).
[4] M. Feliz, G. Ferraudi, H. Miller. *J. Phys. Chem.*, **96**, 257 (1992).
[5] J.R. Shaw, R.H. Schmehl. *J. Am. Chem. Soc.*, **113**, 1991 (1991).
[6] S.A. Moya, J. Guerrero, R. Pastene, R. Schmidt, R. Sariego, R. Sartori, J. Sanz-Aparicio, I. Fonseca, M. Martinez-Ripoll. *Inorg. Chem.*, **33**, 2341 (1994).
[7] R.N. Dominey, B. Hauser, J. Hubbard, J. Dunham. *Inorg. Chem.*, **30**, 4754 (1991).
[8] X. Chen, F.J. Femia, J.W. Babich, J.A. Zubieta. *Inorg. Chem.*, **40**, 2769 (2001).
[9] D.R. Striplin, G.A. Crosby. *Coord. Chem. Rev.*, **211**, 163 (2001).
[10] A.I. Baba, J.R. Shaw, J.A. Simon, R.P. Thummel, R.H. Schmehl. *Coord. Chem. Rev.*, **171**, 43 (1988).
[11] D.R. Striplin, G.A. Crosby. *Chem. Phys. Lett.*, **221**, 426 (1994).
[12] A. Vlcek Jr, J. Heyrovsky. In *Electron Transfer in Chemistry*, V. Balzani (Ed.), Part 2, Vol. 2, p. 804, Wiley-VCH Verlag GmbH, Weinheim (2001).
[13] R. Kia, V. Mirkhani, A. Kalman, A. Deak. *Polyhedron*, **26**, 1711 (2007).
[14] S. Dehghanpour, M. Khalaj, A. Mahmoudi. *J. Coord. Chem.*, **18**, 2957 (2009).
[15] D.D. Perrin, W.L. Armarego, D.R. Perrin. *Purification of Laboratory Chemicals*, 2nd Edn, Pergamon, New York (1990).
[16] G.M. Sheldrick. *SHELXS 97, Program for the Solution of Crystal Structures*, University of Gottingen, Germany (1997).
[17] G.M. Sheldrick. *SHELXL 97, Program for the Refinement of Crystal Structures*, University of Gottingen, Germany (1997).
[18] R. Czerwieniec, A. Kapturkiewicz, J. Lipkowski, J. Nowacki. *Inorg. Chim. Acta*, **358**, 2701 (2005).
[19] N.M. Shavaleev, Z.R. Bell, G. Accorsi, M.D. Ward. *Inorg. Chim. Acta*, **351**, 159 (2003).
[20] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Complexes*, 4th Edn, John Wiley & Sons, USA (1992).
[21] R.W. Balk, D.J. Stufkens, A. Oskam. *J. Chem. Soc., Dalton Trans.*, 1124 (1981).
[22] S. Dehghanpour, M. Khalaj, A. Mahmoudi. *Inorg. Chem. Commun.*, **12**, 231 (2009).
[23] A. Juris, S. Campagna, I. Bidd, J.M. Lehn, R. Ziessel. *Inorg. Chem.*, **27**, 4007 (1988).
[24] R. Lin, T.F. Guarr, R. Duesing. *Inorg. Chem.*, **29**, 4169 (1990).
[25] F. Paolucci, M. Marcaccio, C. Paradisi, S. Roffia, C.A. Bignozzi, C. Amatore. *J. Phys. Chem. B*, **102**, 4759 (1998).