498 **RESEARCH PAPER** SEPTEMBER, 498–501 JOURNAL OF CHEMICAL RESEARCH 2010

Spectroscopic and thermal-gravimetric investigation of two new rhenium (V) ionic liquid complexes

Noura S. AlHokbany* and Refaat M. Mahfouz

King Saud University, Department of Chemistry, College of Science, PO Box 2455, Riyadh, 11451 Kingdom of Saudi Arabia

Rhenium (V) ionic liquids of formula $[BzEt_3N][ReOCl_3$ (MBT)(tri)] and $[Et_3N][ReOCl_3$(amino)] ($BzEt_3N$= benzyltriethyl-ammonuim, Et_3N=triethylammonium, MBT=mercaptobenzothiazole, Tri=1, 2, 4-triazole and amino= amino thiazole) were synthesised by reaction between $[BzEt_3N][ReOCl_4]$ and $[Et_3N][ReOCl_4]$ precursors and free ligands , in the presence of triethylamine. These ionic liquid complexes have been characterised by elemental analysis, spectroscopy (IR, ^{1}H–^{13}C NMR, MS) and thermogravimetric studies. Geometry optimisation of $[Et_3N][ReOCl_3$(amino)] has been carried out using DFT and the predicted IR spectrum of the geometrically-optimised structure shows good agreement with experimental values.

Keywords: rhenium (V) complexes, ionic liquid complexes, thermal properties, DFT calculations

An ionic liquid is a liquid that contains essentially only ions. In the broad sense, the term includes all molten salts, for instance, sodium chloride at temperatures higher than 800 °C. However, the term 'ionic liquid' is now commonly used for salts whose melting point is relatively low (below 100 °C). In particular, salts that are liquid at room temperature are called room-temperature ionic liquids, or RTILs.[1]

Ambient temperature molten salts (ionic liquids) with very low vapour pressure, especially those comprising mixtures of N, N-Φ-dialkylimidazolium (*e.g.*, 1-ethyl-3-methylimidazolium, $[EMIM]^+$, and 1-n-butyl-3-methylimidazolium, $[BMIM]^+$) chloride and aluminum chloride, are increasingly finding a range of laboratory developmental, and technical applications. For example, ionic liquids are used as media for organic and inorganic chemical synthesis, in materials production, in electrochemical and separation processes, and as prototype novel materials. Much current research is focused upon the possible use of ionic liquids as media for cleaner organic synthesis and processing and on better understanding of liquid structure and solvation phenomena of ionic liquids and their relevance to reactivity.[2] Ionic liquids containing transition-metal complexes are of great interest because of their potential catalytic applications. However, relatively few studies have explored the use of ionic liquids for the synthesis and characterisation of coordination complexes. Recently ionic liquids have been used as the media for the preparation of some halometalate complexes and clusters.[1]

In the last decade, room temperature ionic liquids (RTILs) have been used in a variety of catalytic reactions. Their unique physical properties, such as low volatility, low flash point, thermal stability and high polarity make them an attractive alternative to organic solvents.[3] RTILs provide therefore a non-aqueous alternative for two-phase catalysis, in which the catalyst is immobilised in the ionic liquid phase and is easily separated from the products.[3,4] Methyltrioxorhenium (MTO) is a very efficient catalyst precursor for a variety of organic reactions.[5–10]

We now report the synthesis of the new ILs complexes, $[BzEt_3N][ReOCl_3$ (MBT)(Tri)](**1**) and $[Et_3N]$ $[ReOCl_3$(amino)] (**2**). The complexes were characterised using spectroscopy, thermogravimetry and micro analysis. The structure and IR spectra of **2** were calculated using DFT. The investigated complexes could have potential use as selective catalysts or as media for carrying out oxidation–reduction reactions.

Experimental

All chemicals and reagents were used without further purification. Rhenium was purchased from Aldrich as $NaReO_4$ and NH_4ReO_4 and was converted to $[BzEt_3N][ReOCl_4]$ and $[Et_3N]$ $[ReOCl_4]$, as described in the literature.[11,12] Chloroform and methylene chloride were distilled from CaH_2 prior to use. Triethylamine was dried by distillation from CaH_2 and stored over KOH pellets. Methanol was distilled from Mg/I_2 and stored over 3A° molecular sieves. Dry HCl gas was generated as described in Vogel.[13]

IR spectroscopy was recorded on a Perkin Elmer spectrophotometer 1000 in the spectral range 200–4000 cm^{-1} using KBr discs. UV-Vis spectra were recorded on a UV-Vis Beckman Du-70 spectrophotometer in the range 190–700 nm. ^{1}H-^{13}C NMR spectra were measured (DMSO-d_6 and $CDCl_3$ as solvents) on a JOEL-NMR 400 MHz spectrometer. Microanalyses (CHNS) were run at the Mikronalytisches Labor Pascher, Germany. Thermogravimetric/differential thermal analysis (TG/ DTA) measurements were carried out using a Perkin-Elmer TG A7 thermal analyser, the weight loss was measured from ambient temperature up to 1000 °C at a heating rate of 10 °C/min. About 15 mg of the compound was used for the analysis, with alumina as the reference material. Mass spectroscopy was run on a Quattra gas chromotography mass spectrometer at the Mikronalytisches Labor Pascher, Germany.

$[BzEt_3N][ReOCl_3(MBT)(Tri)]$ (**1**): Benzyltriethylammonuim oxotetrachlororehenate (V) (0.11 g, 4.8 mmol) was dissolved in CH_2Cl_2 (5 mL). To this solution was added carefully under constant stirring a mixture of MBT (0.064 g, 0.4 mmol) and Tri (0.0132 g, 0.2 mmol) in CH_2Cl_2 (10 mL). Stirring was continued for 3h and the pH was adjusted by addition of two drops of triethylamine. The solvent was removed by rotary evaporation to almost dryness whereupon a precipitate was obtained. 89% yield of compound, m.p. 67 °C: Anal. Calcd (found) for $C_{22}S_2H_{28}N_5OCl_3Re$: C, 35.9 (36.2); H, 3.81 (4.5); N, 9.53 (10.1); S, 8.71 (8.41); Re, 25.34 (27.3)%. IR (KBr, υ/cm^{-1}): 910 (Re=O), 321 (Re–Cl), 461(Re–S). ^{1}H NMR ($CDCl_3$, ppm): 1.3(t, 9H, CH_3), 2.1 (m, 6H, CH_2), 3.1(t, 2H, CH_2–N), 7.7–7.9 (MBT, H–ph), 8.2(s, CH=N), 7.2–7.4 (Bz, 5H). ^{13}C NMR ($CDCl_3$, ppm): 8.3(CH_3), 45(CH_2), 53(CH_2–Bz), 121, 126, 129, 132(C-ph). UV-Vis (CH_2Cl_2; λ_{max}[nm](ε; $dm^3mol^{-1}cm^{-1}$): 278 (1889) LMCT $\pi(O)\rightarrow d$, 327 (988) assigned to $\pi(Cl)\rightarrow d$. MS(*m/z*)542.7 $[ReOCl_3$(MBT)(Tri)], 167(MBT), 69(Tri).

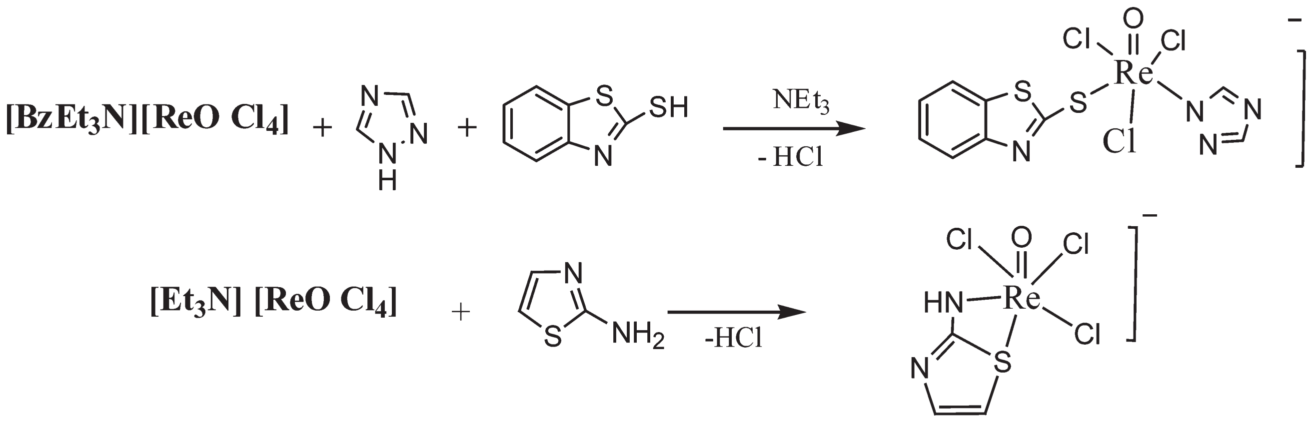
Synthesis of $[Et_3N][ReOCl_3(amino)]$ (**2**): $[Et_3N][ReOCl_4]$ (0.2196 g, 4.63×10^{-4} mmol) was dissolved in MeOH at 0 °C with stirring until the solution became clear green. Amino (0.186 g, 1.853×10^{-3} mmol) was added dropwise to the mixture with continuous stirring at 0 °C whereupon the colour changed to dark red. The solvent was removed by rotary evaporation to almost dryness and a precipitate was obtained. 88% yield of compound, m.p. 88 °C: Anal. Calcd (found) for $C_9H_{18}N_3OCl_3SRe$: C, 21.12 (21.40); H, 3.53 (4.12); N, 8.25 (8.90); S, 6.29 (5.98); Re, 36.6 (37.3) %. IR (KBr, υ/cm^{-1}): 911.1(Re=O), 322 (Re–Cl). ^{1}H NMR (DMSO, ppm):1.15 (t, 9H, CH_3), 2.4 (m, 6H, CH_2), 3.9 (s, NH), 6.6 (d, CH=C), 7(d, CH), 7.7 (s, CH). ^{13}C NMR (DMSO, ppm): 7.6 (CH_3), 51(CH_2), 134(CH=C–N), 107(C–S), 169(C=N). UV-Vis (CH_2Cl_2; λ_{max}[nm](ε; $dm^3mol^{-1}cm^{-1}$) : 273 (3062) due to $\pi(Cl)\rightarrow d$. MS(*m/z*) 407.7$[ReOCl_3$(amino)], 100 (amino).

Results and discussion

The mixed ligand, oxo-complex $[BzEt_3N][ReOCl_3$(MBT)(Tri)] (**1**) has been obtained in high yield by reacting $[BzEt_3N][ReOCl_4]$ with

---

* Correspondent. E-mail: nhokbany@ksu.edu.sa.



Scheme 1

MBT and tri in the presence of base (NEt_3) (see Scheme 1). Complex $[Et_3N][ReOCl_3(amino)]$ (**2**) was obtained by replacement of a chloride ion by the amino-molecule as also shown in Scheme 1.

Microanalytical data showed good agreement between experimentally and theoretically calculated data as included in the experimental section. The key criterion for the evaluation of an ionic liquid is, by definition, its melting point (low temperatures, below 100). Of particular significance is, therefore, the question of the relationship between the structure and chemical composition of an ionic liquid and its melting point.[14,15] In most cases, an increasing size of the anion with the same charge leads to a further decrease in the melting point.[14–17] In general, it can be concluded that the density of comparable ionic liquids decreases as the bulkiness of the organic cation increases.[18,19]

The GAUSSIAN 98 program was used in the calculations.[20] The complex was treated as an open shell-system and no symmetry constraints were applied. Geometrical optimisation of the investigated complex was carried out using Beck's three parameter exchange functional B3LYP using the Los Alamos LANL2DZ spilt-valence basis set,[21,22] and computed following the geometrical optimisation of the complex at the same level of theory (B3LYP) and the same basis set.[22] Natural bond orbital (NBO) calculations were performed using the NBO code[23] included in GAUSSIAN 98.

The calculated bond lengths, bonds angles and torsion angles are in agreement with the values based upon the X-ray crystal structure data for other oxo-rhenium complexes of comparable structure as shown in Table 1.[24]

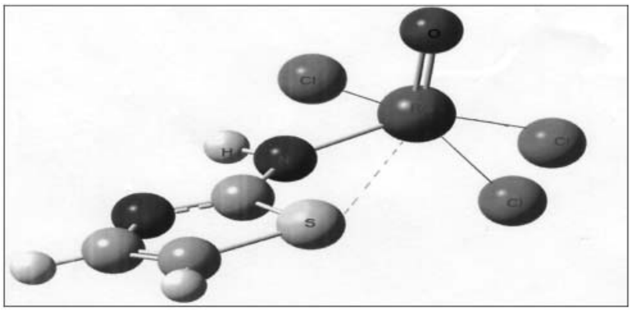


Fig. 1 Optimised structure of (**2**).

Table 1 Optimised bond length(A^0) for (**2**)

Bond length (A^0)	B3LYP/LANL2DZ	Experimental x-ray data of comparable $[ReOCl_3(bpzm)]$.[24]
Re(1)–O(2)	1.6952	1.6973
Re(1)–Cl(3)	2.4547	2.4502
Re(1)–N(6)	1.8907	2.0089

Table 2 Atomic charges from the natural population anaylsis (NPA) for (**2**)

Atom	Atomic charge
Re(1)	0.5680
Cl(3)	–0.227
N(6)	–0.610
O(2)	–0.418
Cl(4)	–0.264

Table 2 presents the atomic charges from the Natural Population Analysis (NPA) for for (**2**). The calculated charge on the rhenium atom was found to be considerably lower than the formal charge of +5, as a result of significant charge donation from the chloride ions and the N-ligand. The charge on the oxo ligand is significantly smaller than (2^-) and less negative than the charge on the Cl ligand (–1), which indicates high electron density delocalisation.[25]

The Re centre of anionic (**2**) is less positive in comparison with other complexes of rhenium,[26] as a result of the σ-donation from three chloride atoms towards the Re in this anionic complex. It indicates higher electron density delocalisation from these ligands towards to the rhenium centre and corresponds to differences in the Re-charge.

Table 3 compares the calculated and observed vibrational modes of (**2**). It should be mentioned that the theoretical values are usually higher than the experimental data. One has to scale the theoretical data by optimal scaling factors which vary by basis set. In our case quite good agreement between the theoretical and experimental data was detected.

The IR spectrum of complex (**1**) displays the characteristic bands of the cation part, namely the C–H and C–C out-of plane bending vibrations in the mono-substituted benzene ring in the 604–750 cm^{-1} region and the υ(C=C) stretching vibrations at 1456 cm^{-1}. Some bands in the complexes spectrum are absent, with respect of the free ligands, such as the donor sets SH and NH_2 at 2889 and 3408 cm^{-1} respectively, indicating that these donor atoms were deprotonated upon complexation. The IR spectra of (**1**) and (**2**) exhibit also characteristic υ(Re=O) stretching bands at 910, 911 cm^{-1}, respectively, which are in the range reported for the precursor $ReOCl_4^-$.[27]

Resonances observed in the range 1–4 δ are attributed to the aliphatic protons of the $BzEt_3N$ cation. The multiplet signals arising from the benzyl ring protons are in the range 7.5–7.51 δ. The $[Et_3N]$

Table 3 Calculated and observed vibrational modes of (**2**)

Experimental	B3LYP/LANL2DZ	Assignment
910	959.6	νRe=O
322	350	νRe-Cl
561	680	νRe-N
1520	1579	υC=C
1623	1647	υC=N

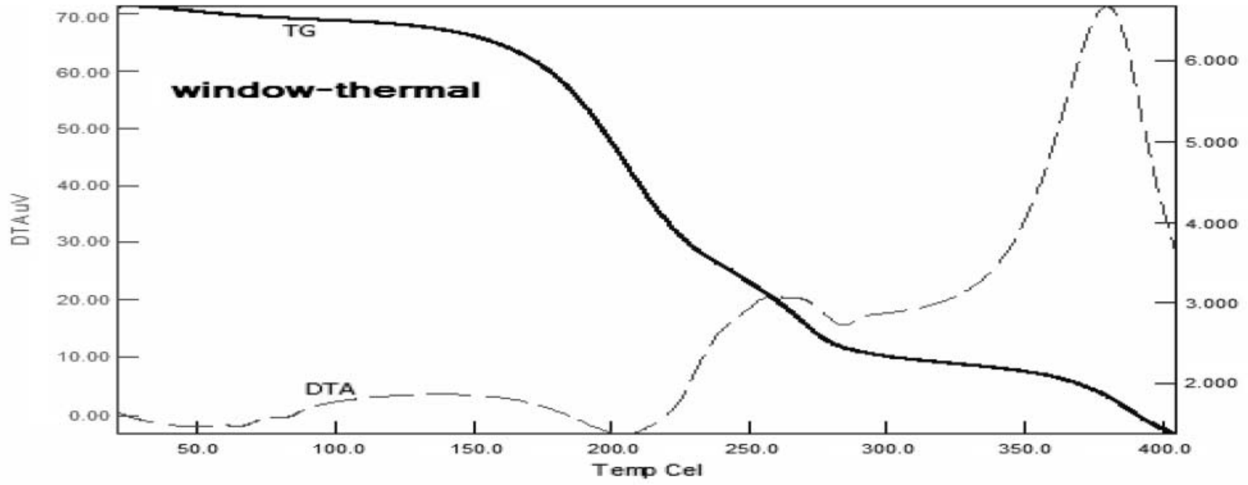


Fig. 2 Thermogram of complex **1.**

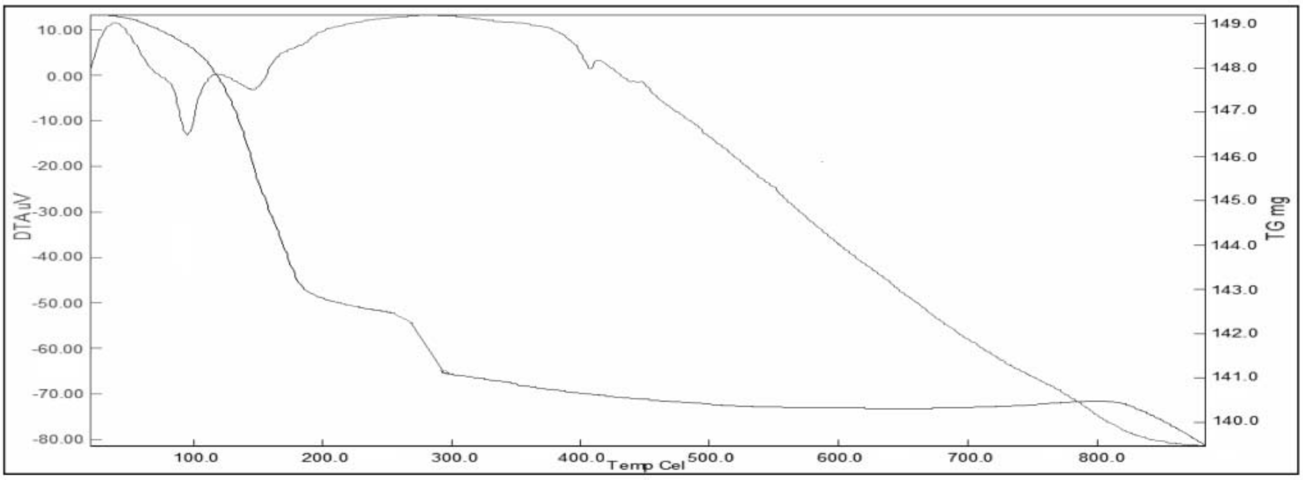


Fig. 3 TG curve of complex **2**.

cation exhibits signals of aliphatic protons with some downfield shift in complex **2**. In complex **1** the protons of the benzene ring of [$BzEt_3N$] overlap with those of the benzene ring of MBT. The MBT protons at 7.7–7.9 are more deshielded being nearer to the oxo core[28] than the benzene ring of the cation. The ^{13}C NMR spectrum (ppm) indicated the presence of *ipso*-carbon atoms of aromatic ring at $\delta = 133.1$ and *ortho*-carbon atoms at 130.0, the signals at 129.0 are due to *meta*-carbon atoms and the *para*-carbon resonates at 128.4. The aliphatic group resonances are at 16.0, 17.0 (CH_3), 52.0 (CH_2), and 60.0 (CH_2–N). The investigated complexes exhibit two characteristic C–S and C–N signals at lower field compared to those of the ligands, indicating that coordination is *via* the charged thiolate sulfur atom. The SH signals of each bidentate ligands disappear upon coordination and the associated C–S and C–N carbons signals are deshielded at 133.0 and 143.0 ppm *versus* 137.0, and 148.0 ppm in the free ligands, confirming that coordination is also through the S site.

The mass spectra of the investigated complexes show two major peaks with *m/z* at 542.7 and 407.7 attributed to anionic species of **1** and **2**, respectively. For complex **1**, three fragments at 180, 167 and 68 *m/z*, were ascribed to $[ReO]^{3+}$, (MBT) and (tri) species, respectively. In case of complex **2** a fragment of *m/z* 100 corresponded to the (amino) fragment.

The electronic absorption spectra of the complexes in dichloromethane were recorded at room temperature. A broad strong absorption was observed in the range 260–340 nm, which is a characteristic band of oxorhenium (V) complexes and is due to charge transfer from the ligand to the metal ion.[29]

Figure 2 shows typical TG/DTA curves of compound **1**. The TG curve exhibits a TG-window for ionic liquids in temperature range 25–170 °C and two overlapped decomposition steps. The first weight loss of (28.9%) occurs in the temperature range of 150–220 °C, which can be ascribed to the loss of cation species $BzEt_3N$ (calculated value 26%). This weight loss was accompanied by an endothermic peak maximised at 220 °C. The successive weight losses in the temperature range of 220–320 °C, could be attributed to losses of three chloride ions, MBT and Tri moieties. A minor weight gained was observed in the range of 350–380 °C attributed to oxidation process and formation of Re_2O_3. The oxidation process was probably accompanied by an exothermic peak as shown in DTA curve.

The thermal behaviour of the compound **2** displays, in addition to the TG-window for ionic liquids in the temperature range 25–120 °C, two collapse-stages as shown in Fig. 3. The first weight loss of 20.2% occurred in the temperature range of 120–180 °C, and attributed to the loss of [Et_3N] molecules. The second decomposition step, detected in the temperature range of 200–320 °C, is ascribed to loss of ligands. The two endothermic processes were maximised at 120 °C and 210 °C as shown in the DTA curve.

Conclusion

Ionic liquids (ILs) have attracted interest as reaction media for organic reaction, for extraction, and as potential catalysts. In this respect we have synthesis two new oxorhenium (V) ionic liquids of potential use in the field of nuclear pharmacy and catalytic application of metal complexes. The chemical formula of two compounds deermined by chemical and physical measurements reported in this investigation and a DFT computional study was carried out one of the investigated ILs.

Received 20 December 2009; accepted 28 July 2010
Paper 090922 doi: 10.3184/030823410X12828399425330

References

1 J. Joni, D. Schmitt, P.S. Schulz, T.J. Lotz and P. Wasserscheid, *J. Catalysis*., 2008, **258**, 401.
2 G.S. Owens, J. Arias and M.M. Abu-Omar, *Catalysis Today*, 2000, **55**, 317.
3 D. Betz, W.A. Herrmann, and F.E. Kühn, *J. Org.Chem.*, 2009, **130**, 5.
4 P. Paraskevopoulou, N. Psaroudakis, S. Koinis, P. Stavropoulos and K. Mertis, *J. Molec. Catalysis A: Chem.*, 2005, **240**, 27.
5 S. Zang, D-W.F. Jianxin, L.Y-Yang Zhang and S. Yue, *Fluid Phase Equilibria.*, 2009, **205**, 21.
6 Z. Yang, C.-F. Ma, X.-S. Lin, J.-T. Yang and T.-M. Guo, *Fluid Phase Equilibria*, 1999, **157**, 143.
7 D.-W. Fang, W. Guan, J. Tong, Z.-W. Wang and J.-Z. Yang, *J. Phys. Chem. B* 2008, **112**, 7499.
8 J. Tong, Q.-S. Liu, W.-G. Xu, D.-W. Fang and J.-Z. Yang, *J. Phys. Chem. B*, 2008, **112** (**14**), 4381.
9 J. Tong, Q.-S.Liu, W.Guan, and J.-Z.Yang, *J. Phys. Chem.*, 2007, **B 111**, 3197.
10 W. Tong, H. Song, C. Gao, and H. Möhwald, *J. Phys. Chem. B*, 2006, **110** (**26**), 12905.
11 T. Fietz, H. Spies, H.-J. Pietzsch and P. Leibnitz, *Inorg.Chim.Acta*., 1995, **231**, 233.
12 T. Lis and B. Jeżowska-Trzebiatowska, *Acta.Cryst*., 1977, **B33**, 1248.
13 A.I. Vogel, *Text of practical organic chemistry*, 5 edn, 1989.
14 M. Glaser, M.J. Howard, K. Howland, A.K. Powell, M.T. Rae, S. Wocadlo, R.A. Williamson and P.J. Blower, *J. Chem. Soc. Dalton Trans*., 1998, 3087.
15 J. ONeil, S. Wilson and J. Katzenellenbogen, *Inorg. Chem*., 1994, **33**, 319.
16 M. Akbar Ali, R.J. Butcher and J.C. Bryan., *Inorg. Chim. Acta.*, 1999, **287**, 8.
17 A.R. Choudhury, N. Winterton, A. Steiner, A.I. Cooper and K.A. Johnson, *J. Am. Chem. Soc*., 2005, **127**, 16792.
18 H. Stegemann, A. Rohde, A. Reiche, A. Schnittke and H. Füllbier, *Electrochim. Acta.*, 1992, **37**, 379.
19 Gaussian 98 program, Gaussian, Inc. Pittsburgh. PPA 15106 USA.
20 A.D. Becke, *J. Chem. Phys. Lett*., 1995, **233**, 134.
21 R.G. Parr and S. Liu, *J. Mol. Struct. Theochem*., 2000, 29–34.
22 P.J. Hay, S.P. Chen, A.F. Voter, R.C. Albers and A.M. Boring, *Scripta Metall*, 1989, **23**, 217.
23 E.D. Glendening, A.E. Reed, J.E. Carpenter and F. Weinhold, NBO (version 3.1).
24 B. Machura, R. Kruszynski and J. Kusz, *Polyhedron*., 2007, **26**, 2581.
25 B. Machura, R. Kruszynski, and J. Kusz, *Polyhedron*., 2008, **27**, 1679.
26 B. Machura, R. Kruszynski, M. Jaworska and P. Lodowski, *Polyhydedron*., 2005, **24**, 1454.
27 T. Nicholson, J. Cook, A. Davison, D.J. Rose, K.P. Maresca, J.A. Zubieta and A.G. Jones, *Inorg. Chim. Acta*., 1996, **252**, 421.
28 T. Nicholson, J. Cook, A. Davison, D.J. Rose, K.P. Maresca, J.A. Zubieta and A.G. Jones, *Inorg. Chim. Acta*., 1996, **297**, 427.
29 B. Machura, *Coord. Chem. Rev*., 2005, **249**, 591.