ELSEVIER

Coordination Chemistry Reviews
208 (2000) 77–86

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Excited-state properties of ruthenium(II) polypyridyl complexes containing asymmetric triazole ligands

Stefano Fanni [a], Tia E. Keyes [b], Christine M. O'Connor [a],
Helen Hughes [a,1], Renyi Wang [a,2], Johannes G. Vos [a,*]

[a] *Inorganic Chemistry Research Centre, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland*
[b] *School of Chemistry, Dublin Institute of Technology, Dublin 8, Ireland*

Received 17 September 1999; accepted 15 December 1999

Contents

Abstract

The photochemical and photophysical properties of ruthenium polypyridyl complexes containing 1,24-triazole-based ligands, such as pyridine- and pyrazine triazoles are reviewed. The excited-state behaviour of such complexes is discussed in relation to the asymmetry inherently present in these ligands. For the pyridine triazole-containing complexes a series of photochemically induced isomerisations is reported. Pyrazine triazole compounds show a

---

* Corresponding author. Tel.: +353-1-704 5307; fax: +353-1-704 5503.
E-mail address: han.vos@dcu.ie (J.G. Vos).
[1] Present address: Department of Chemistry, Waterford Institute of Technology, Waterford, Ireland.
[2] Present address: Shipley-Ronal Division, Rohm and Haas, 2631 Michelle Drive, Tustin, CA 92780, USA.

PII: S0010-8545(00)00245-9

very unusual dual emission, which has been investigated using temperature dependent emission lifetime studies and partial deuteriation.

Keywords: Ruthenium; Excited states; Photochemistry; Triazole

---

1. Introduction

Over the past two decades ruthenium(II) polypyridyl chemistry has become an area of extensive inquiry in inorganic research. The driving force behind these investigations has been the potential application of such complexes as building blocks in supramolecular devices due to their favourable excited state and redox properties [1]. Importantly, variation of, or modifications to, the ligands coordinated to the ruthenium centre can tune these properties to create a desired effect. The synthetic methodology behind such design is well developed and there are very few examples of metal ions that offer similar synthetic flexibility. Many of the complexes prepared in these studies have the general formula $[Ru(bpy)_2(L)]^{2+}$, where bpy is 2,2′-bipyridyl and L another chelating ligand. Complexes containing polypyridyl ligands other than bpy have also been reported. In the majority of compounds L is a bis-chelating ligand where both arms have identical coordination properties. We have over the last number of years carried out systematic investigations on asymmetric chelating ligands [2]. The chelating ligands used in these studies are based on substituted 1,2,4-triazole moieties. Some of these ligands are shown in Fig. 1. Haga and co-workers have also reported on a series of related compounds based on imidazole rings [3]. The aim of these studies has been to

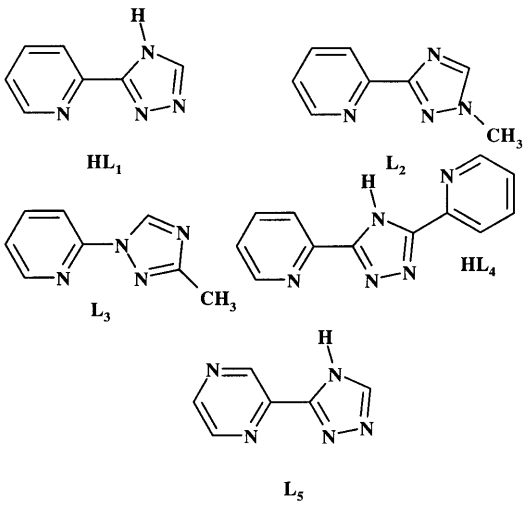


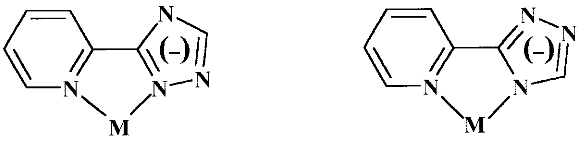
Fig. 1. Ligand structures.

investigate the effect of asymmetry on the photophysical properties of the ruthenium polypyridyl compounds. The synthetic flexibility of the triazole moiety lends itself to a systematic investigation into the nature of excited states of its complexes. Variations in composition that can be achieved include: varying the substitution pattern of the triazole ring, the attachment of pendent groups and variation of the nature of the adjoining chelating group ring, e.g. pyridine or pyrazine (Fig. 1). In this contribution we review work which considers the effect of a series of pyridine and pyrazine triazole ligands on the photochemistry and photophysics of ruthenium polypyridyl complexes. Particular attention will be paid to the photochemical properties of mononuclear compounds and a number of photoinduced isomerisation reactions are presented. The location of the excited state in these compounds will also be discussed.

2. Results and discussion

2.1. General synthetic considerations

Before discussing the excited-state properties of Ru(II) compounds based on pyridine or pyrazine triazole ligands the coordination properties of the triazole moiety must be considered. Triazoles contain a acidic N–H group, which imparts unusual properties to the ligands discussed here. In the deprotonated state the ligand is a strong σ-donor while the second, pyridine or pyrazine, arm of the chelating ligand has well defined π-acceptor properties. The two coordinating arms of the ligand therefore possess quite different electronic properties. Furthermore, two binding positions are available on the triazole ring, namely N2 and N4 (Fig. 2), these sites are not equivalent and therefore introduce further asymmetry into the metal complex. The extent to which N2 or N4 is coordinated during reaction with a Ru(bpy)$_2$ unit depends on the presence of substituents on the triazole (Fig. 1). Chromatographic techniques have been developed to separate these coordination isomers and their nature [4] has been established by ^{1}H NMR and X-ray crystallography. It has been shown that in dinuclear complexes based on pyridine and pyrazine triazole ligands the negative charge on the triazole ring greatly affects the interaction between the metal centres [5]. In this overview we will consider however, only mononuclear complexes.



N2 isomer **N4 isomer**

Fig. 2. Different coordination modes of 1,2,4-triazoles.

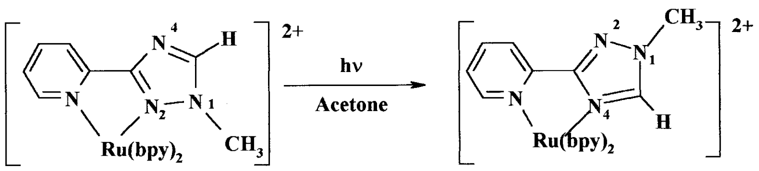
2.2. Pyridine triazole complexes

In mixed-ligand metal complexes of this type it is important to determine the nature of the emitting state. Emission in ruthenium polypyridyl complexes occurs from a triplet metal-to-ligand-charge-transfer (^{3}MLCT) state. In a mixed-ligand species, this state can be based on the polypyridyl ligand or on L. Detailed resonance Raman studies, excited state pK_a measurements and isotopic labelling studies have shown that for the pyridine triazole complexes this emitting state is bpy-based, irrespective of the state of protonation of the triazole ring. The acid–base behaviour of the triazole has a profound effect on the photochemical behaviour [6] of the complex $[Ru(bpy)_2L_1]^+$. Studies of the temperature dependence of the emission from $[Ru(bpy)_2L_1]^+$ indicate that thermal population of the deactivating ^{3}MC state does not occur (Arrhenius parameters for the N2 isomer; pre-factor 4.7×10^7 s^{-1} and activation energy 550 cm^{-1}) consequently the compound is photostable. This photostability is most likely caused by the strong σ-donor properties of the deprotonated triazole ligand, which induces strong ligand field splitting in the complex. The energy gap between the bpy excited state and ^{3}MC level is therefore increased and this level may not be populated at room temperature (r.t.) from the excited ^{3}MLCT state. The σ-donor properties of the triazolate are so strong that even in the presence of strongly π-accepting 2,2′-biquinoline ligands photostable compounds may be prepared [7].

Upon protonation of the triazole ring the complex $[Ru(bpy)_2(HL_1)]^{2+}$ is obtained and the temperature dependence studies of the emission of this compound (Arrhenius parameters for the N2 isomer; pre-factor 6.0×10^{10} s^{-1} and activation energy 1710 cm^{-1}) clearly indicate that population of the ^{3}MC level is occurring. This state is dissociative and as a result the compound is expected to be photolabile. Photochemical investigations have indeed shown that in dichloromethane in the presence of Cl^- loss of the HL_1 ligand is observed. In pure dichloromethane a more interesting behaviour is taking place. Detailed HPLC measurements have shown that in pure CH_2Cl_2, photochemically induced coordination isomerisation of the triazole ligand occurs. Continuous irradiation of the pure N2 isomer leads to a steady-state where the N4:N2 ratio is 4:1 (Fig. 3). Irradiation starting from the N4 isomer gives the same steady-state ratio. This observation suggests that upon photolysis a monodentate intermediate is formed where HL_1 is coordinated to the metal centre by the pyridine ring, followed by rotation of the triazole ring.

A different behaviour [8] is observed for $[Ru(bpy)_2L_2]^{2+}$. For this complex two different isomers can be prepared. Upon the reaction of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ with L_2 the N4 coordinated isomer is obtained as the single product. The presence of the methyl group on N1 prevents the formation of the N2 isomer. However, when the complex $[Ru(bpy)_2(L_1)]^+$ is directly methylated the N2 isomer can be obtained in high yield.

Photolysis in acetone shows that the N4 isomer is photostable, while for the N2 isomer fast photoinduced isomerisation to the N4 isomer is observed (see reaction 1).



(1)

So contrary to the HL_1 case the photoinduced isomerisation is not reversible, the sterically most favoured N4 compound, is obtained as the single product.

A different photoinduced transformation is observed [9] for $[Ru(bpy)_2L_3]^{2+}$. During irradiation of this complex in acetonitrile or in acetonitrile-containing LiCl, the absence of a set of isosbestic points in the UV–vis spectra suggested the presence of an intermediate. Preparative photolysis followed by HPLC separation lead to the isolation of two products in which the metal center is coordinated in a

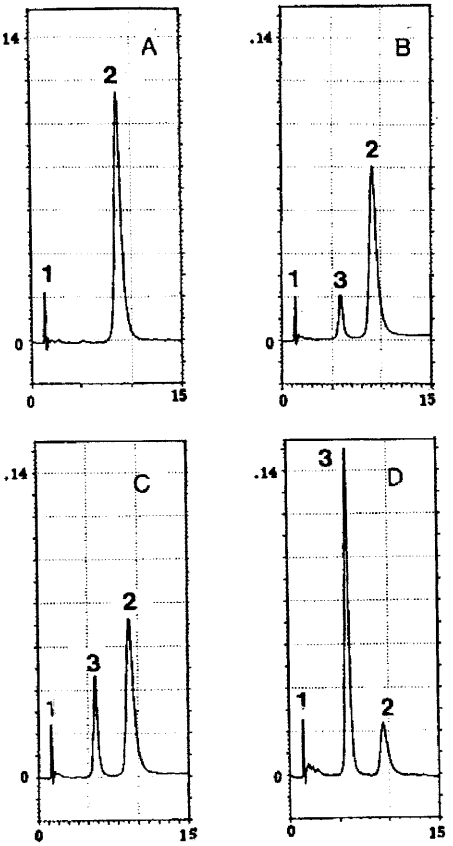


Fig. 3. HPLC traces of the photolysis of $[Ru(bpy)_2(HL_1)]^{2+}$ in CH_2Cl_2: A, 0 min; B, 10 min; C, 20 min; and D, 200 min. Peak 1 is CH_2Cl_2, 2 is N2 isomer and 3 is N4 isomer.

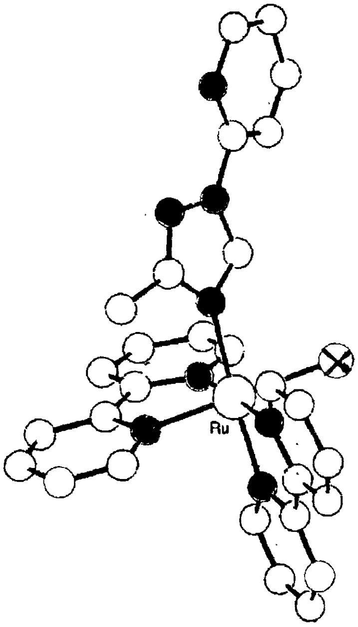


Fig. 4. Structure of $[Ru(bpy)_2(L_3)Cl]^+$ (●) is nitrogen, (⊗) is chloride.

monodentate fashion to the pyridyltriazole ligands. In pure acetonitrile $[Ru(bpy)_2(L_3)CH_3CN]^{2+}$ was obtained as in reaction 2:

$$[Ru(bpy)_2(L_3)]^{2+} + CH_3CN \xrightarrow{hv} [Ru(bpy)_2(L_3)(CH_3CN)]^{2+} \tag{2}$$

while in the presence of LiCl the singly charged $[Ru(bpy)_2(L_3)Cl]^+$ species was obtained as a second intermediate (reaction 3):

$$[Ru(bpy)_2(L_3)]^{2+} + Cl^- \xrightarrow{hv} [Ru(bpy)_2(L_3)Cl]^+ \tag{3}$$

The end products in these reactions are as expected $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ and $[Ru(bpy)_2(CH_3CN)Cl]^+$.

The composition of the initial photoproducts $[Ru(bpy)_2(L_3)(CH_3CN)]^{2+}$ and $[Ru(bpy)_2(L_3)Cl]^+$ suggests that the ligand L_3 is coordinated in a monodentate fashion. X-ray crystallography was used to identify the coordination mode of the ligand L_3 in these compounds and it was found that in $[Ru(bpy)_2(L_3)Cl]^+$ the monodentate coordinated ligand is bound to the triazole ring and that a ring slippage has taken place (Fig. 4). NMR evidence suggests that for the acetonitrile analogue the same coordination mode is obtained.

Further photolysis of the $[Ru(bpy)_2(L_3)(CH_3CN)]^{2+}$ complex in acetone leads very surprisingly to the reformation of the parent $[Ru(bpy)_2(L_3)]^{2+}$ compound. This shows that, upon photolysis of the compound in a strongly coordinating solvent such as acetonitrile a solvent adduct is obtained, while in weakly coordinating solvents photochemically induced chelation occurs. It is important to note here that,

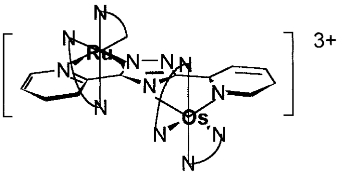


Fig. 5. Structure of dinuclear mixed-metal Ru/Os complex of L_4^-.

contrary to what is observed for the HL_1 complex, in the L_3 compound the monodentate ligand is coordinated to the triazole ring and that ring slippage has occurred.

In the literature, monodentate intermediates have often been proposed in photochemically induced ligand exchange reactions, although such intermediates are seldom isolated. The only other example to our knowledge is reported by Tachiyashiki and co-workers who observed monodentate coordinated 3,3′-dimethyl-2,2′-bipyridyl and 2-aminomethylpyridine after irradiation of the corresponding $Ru(bpy)_2$ complexes [10]. It seems therefore that with the use of asymmetric ligands, monodentate intermediates can be stabilised and isolated.

It was highlighted above that because of their negative charge, bridging triazolates promote interaction between different metal centres in dinuclear species. This property in relation to mixed-valence compounds has been addressed in a previous review [11]. The triazolate supports photoinduced energy transfer, through what is believed to be a Dexter electron exchange mechanism. For example in mixed-metal ruthenium/osmium polypyridyl complexes with the bridging ligand L_4^- (Fig. 5) only osmium-based emission is observed [5]. This ability to promote interaction between reactive components over a negatively charged bridge is also observed in a phenothiazine substituted pyridine triazole complex (Fig. 6). In this molecule fast electron transfer from the phenothiazine grouping to the ruthenium centre is observed when the complex is irradiated in acetonitrile and in the presence of methylviologen as electron acceptor [12].

2.3. Pyrazine triazole complexes

As outlined above, in mixed-ligand complexes of this type the location of the emitting triplet state is an important factor. For pyrazine triazole-containing complexes,

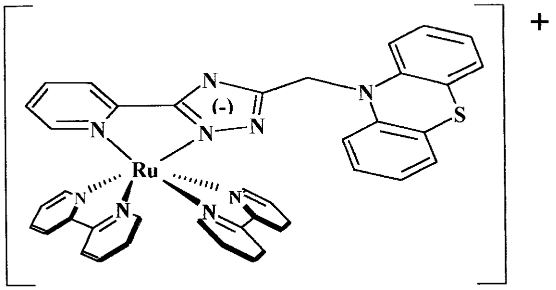


Fig. 6. Structure of ruthenium phenothiazine dyad.

such as $[Ru(bpy)_2(L_5)]^+$ the situation is more complicated than for the analogous pyridine triazole compounds. Time-resolved resonance Raman measurements and acid–base investigations indicate that the emitting state is bpy-based when the triazole ring is deprotonated but that for $[Ru(bpy)_2(HL_5)]^{2+}$, when the triazole is protonated, the emitting state switches to the pyrazine moiety [13]. Additional evidence to support this conclusion was obtained recently using partial deuteriation of these complexes [14]. Previous experiments suggested that deuteriation of a ligand will only affect the emission lifetime of a compound when this ligand is directly involved in the emission process. Deuteriation of spectator ligands should not therefore influence the emission quantum yield or lifetime. In agreement with this model an increase of the emission lifetime of the pyridine triazole complexes is only observed upon deuteriation of the polypyridyl ligands, irrespective of the protonation-state of the triazole ring. For $[Ru(bpy)_2(HL_5)]^{2+}$, deuteriation of the polypyridyl ligands does not affect the emission, but deuteriation of HL_5 leads to a twofold increase of emission lifetime. This indicates that when the triazole is protonated the emission is indeed pyrazine-based. Surprisingly however, when the triazole ring is deprotonated deuteriation of either bpy or L_5^- has little influence on emission lifetime at r.t. Temperature dependent emission studies between 120 and 200 K suggest that this unexpected result may be explained by the presence of two

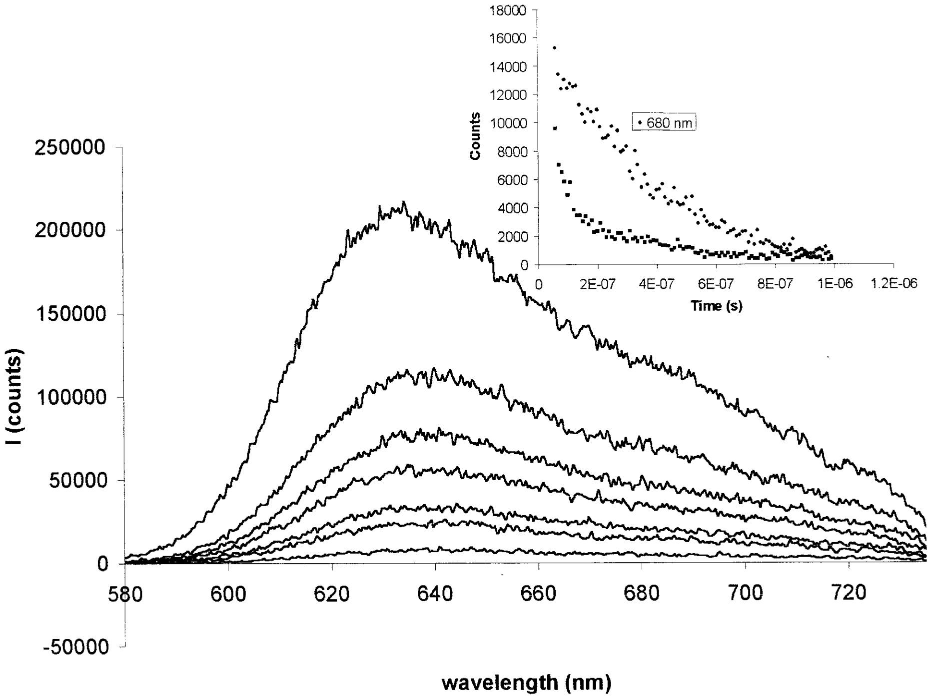


Fig. 7. Time-resolved emission spectra of $[Ru(bpy)_2(L_5)]^+$ in methanol/ethanol, 4:1, and 1% diethylamine at 140 K (inset: decay profiles monitoring at 610 (bottom) and 680 nm (top).

weakly coupled exciting states, which are clearly visible as two emission signals at about 620 (pyrazine-based) and 680 (bpy-based) nm. The main decay pathways are deactivation of the pyrazine-based triplet state via the ^{3}MC state by tunnelling and on non-radiative processes. This limits the influence isotopic substitution has on the emission lifetimes of such complexes. The time-resolved emission spectra obtained for $[Ru(bpy)_2(L_5)]^+$ at 140 K are shown in Fig. 7. The insert reveals the different kinetic behaviour for each component of the emission at this temperature. The two excited states also exhibit different temperature dependence. The data from temperature dependence emission studies also show that lifetimes are relatively unaffected by ligand deuteriation over a substantial temperature range. The protonated analogue of the same complex, $[Ru(bpy)_2(HL_5)]^{2+}$ exhibits a 'normal' emission spectrum with a single maximum and mono-exponential luminescent decay.

Deactivation of the higher energy, pyrazine-based level occurs through the ^{3}MC state, the fitting of temperature dependent data suggests that the pyrazine-based ^{3}MLCT is at equilibrium with the deactivating ^{3}MC state.

3. Conclusions

The investigation of the photochemical and photophysical properties of asymmetric triazole-based ruthenium polypyridyl complexes has clearly shown that with asymmetric ligands interesting and unusual photochemical and photophysical behaviour can be obtained. The results show that this behaviour can be manipulated by synthetic variation in the ligand structures. It has also been shown that with the presence of a potentially negatively charged triazole ring energy- and electron-transfer processes can be controlled. Finally, the use of partial deuteriated metal complexes has highlighted an unexpected wealth of photophysical properties for these compounds. Detailed investigations are in progress at the moment to further investigate the intriguing photophysics of these, simple, mononuclear complexes.

Acknowledgements

SF and JGV thank the EC TMR Programme (grant no. CT96-0031) for financial assistance.

References

[1] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, Chem. Rev. 96 (1996) 759.

[2] (a) R. Hage, A.H.J. Dijkhuis, J.G. Haasnoot, R. Prins, J. Reedijk, B.E. Buchanan, J.G. Vos, Inorg. Chem. 27 (1988) 2185. (b) R. Hage, R. Prins, J.G. Haasnoot, J. Reedijk, J.G. Vos, J. Chem. Soc. Dalton Trans. (1986) 253. (c) B.E. Buchanan, J.G. Vos, M. Kaneko, W.J.M. van der Putten, J.M. Kelly, R. Hage, R. Prins, J.G. Haasnoot, J. Reedijk, R.A.G. de Graaff, J. Chem. Soc. Dalton Trans. (1990) 2425. (d) R. Hage, J.G. Haasnoot, D.J. Stufkens, T.L. Snoeck, J.G. Vos, J. Reedijk, Inorg. Chem. 28 (1989) 1413.

[3] (a) T. Ohno, K. Nozaki, M-A Haga, Inorg. Chem. 31 (1992) 4256. (b) T. Ohno, K. Nozaki, M-A Haga, Inorg. Chem. 31 (1992) 548. (c) M-A Haga, Md M. Ali, S. Koseki, K. Fujimoto, A. Yoshimura, K. Nozaki, T. Ohno, K. Nakajima, D.J. Stufkens, Inorg. Chem. 35 (1996) 3335.

[4] (a) B.E. Buchanan, E. McGovern, P. Harkin, J.G. Vos, Inorg. Chim. Acta 154 (1988) 1. (b) B.E. Buchanan, R. Wang, J.G. Vos, R. Hage, J.G. Haasnoot, J. Reedijk, Inorg. Chem. 29 (1990) 3263.

[5] (a) R. Hage, A.H.J. Dijkhuis, J.G. Haasnoot, R. Prins, J. Reedijk, B.E. Buchanan, J.G. Vos, Inorg. Chem. 27 (1988) 2185. (b) R. Hage, J.G. Haasnoot, H.A. Nieuwenhuis, J. Reedijk, D.J.A. De Ridder, J.G. Vos, J. Am. Chem. Soc. 112 (1990) 9245. (c) L. De Cola, F. Barigelletti, V. Balzani, R. Hage, J.G. Haasnoot, J. Reedijk, J.G. Vos, Chem. Phys. Lett. 178 (1991) 491.

[6] R. Wang, J.G. Vos, R.H. Schmehl, R. Hage, J. Am. Chem. Soc. 11 (1992) 1964.

[7] T.E. Keyes, J.G. Vos, J.A. Kolnaar, J.G. Haasnoot, J. Reedijk, R. Hage, Inorg. Chim. Acta 245 (1996) 237.

[8] S. Fanni, S. Murphy, J.S. Killeen, J.G. Vos, Inorg. Chem. 39 (2000) 1320.

[9] (a) B.E. Buchanan, H. Hughes, J. van Diemen, R. Hage, J.G. Haasnoot, J. Reedijk, J.G. Vos, J. Chem. Soc. Chem Commun. (1991) 300. (b) H. Hughes, P. Degn, J.M. Pavon Velasco, B.S. Creaven, C. Long, J.G. Vos, R.A. Howie, R. Hage, J.H. van Diemen, J.G. Haasnoot, J. Reedijk, J. Chem. Soc. Dalton Trans. (1992) 1177.

[10] (a) S. Tachiyashiki, H. Ikezawa, K. Mizumachi, Inorg. Chem. 33 (1994) 623. (b) R.Arakawa, S. Tachiyaskiki, T. Matsuo, Anal. Chem. 67 (1995) 4138.

[11] R. Hage, J.G. Haasnoot, J. Reedijk, J.G. Vos, Chemtracts, Inorganic Chemistry, March/April,1992, p. 75.

[12] S. Fanni, T.E. Keyes, S. Campagna, J.G. Vos, Inorg. Chem. 37 (1998) 5933.

[13] (a) H.A. Nieuwenhuis, J.G, Haasnoot, R. Hage, J. Reedijk, T.L. Snoeck, D.J. Stufkens, J.G. Vos, Inorg. Chem. 30 (1991) 48. (b). R. Hage, J.G. Haasnoot, H.A. Nieuwenhuis, J. Reedijk, R. Wang, J.G. Vos, J. Chem. Soc. Dalton Trans. (1991) 3271. (c) C.G. Coates, T.E. Keyes, J.J. McGarvey, H.P. Hughes, J.G. Vos, P.M. Jayaweera, Coord. Chem. Rev. 171 (1998) 323. (d) C.G. Coates, T.E. Keyes, H.P. Hughes, P.M. Jayaweera, J.J. McGarvey, J.G. Vos, J. Phys. Chem. 102 (1998) 5013.

[14] T.E. Keyes, C.M. O'Connor, U. O'Dwyer, C.G. Coates, P. Callaghan, J.J. McGarvey, J.G. Vos, J. Phys. Chem. A. 103 (1999) 8915.