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Synthesis, structure and spectroscopic properties of novel metal–metal bonded manganese–ruthenium complexes with α -diimine ligands. X-ray structure of $[(\text{CO})_5\text{Mn}-\text{Ru}(\text{Me})(\text{CO})_2(\sigma(\text{N}),\sigma(\text{N}'))\text{-iPr-PyCa}]$ (iPr-PyCa = pyridine-2-carbaldehyde-*N*-isopropylimine)

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Abstract

The synthesis and spectroscopy of the complexes $[(\text{CO})_5\text{Mn}-\text{Ru}(\text{Me})(\text{CO})_2(\alpha\text{-diimine})]$ (α -diimine = *N,N'*-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB), pyridine-2-carbaldehyde-*N*-isopropylimine (iPr-PyCa)) are reported. The metal fragments are bonded to each other by an uncommon manganese–ruthenium bond. The single crystal X-ray structure has been determined. The purple crystals of $[(\text{CO})_5\text{Mn}-\text{Ru}(\text{Me})(\text{CO})_2(\text{iPr-PyCa})]$ are monoclinic, space group $P2_1/n$, $Z=4$, with unit cell dimensions $a=9.6297(7)$, $b=20.923(1)$, $c=10.166(1)$ Å and $\beta=92.190(8)^\circ$. The structure refinement converged to $R=0.035$ for 3277 observed reflections. Both complexes show a strong, solvatochromic absorption band in the visible region, which is assigned to Ru(d_π) $\rightarrow$ α -diimine (π^*) transitions. In agreement with this assignment, the Raman spectra show resonance enhancement of Raman intensity for $\nu_s(\text{CO})$ and $\nu_s(\text{CN})$ of the $\text{Ru}(\text{Me})(\text{CO})_2(\alpha\text{-diimine})$ fragment.

Keywords: Crystal structures; Manganese complexes; Ruthenium complexes; Diimine complexes; Carbonyl complexes

1. Introduction

Few dinuclear organometallic complexes are known in which the metal–metal bond is the only link between two metal fragments, e.g. $[\text{M}_2(\text{CO})_{10}]$ ($\text{M}=\text{Mn}, \text{Re}$), $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ and $[\text{M}_2\text{Cp}_2(\text{CO})_6]$ ($\text{M}=\text{Mo}, \text{W}$) [1–3]. Irradiation leading to the metal–metal bonding to anti-bonding electronic transition ($\sigma_b \rightarrow \sigma^*$) results in an efficient photodecomposition of the complex. Highly coloured complexes are obtained if two carbonyls are substituted by a ligand with a low-lying π^* -orbital, such as an α -diimine. Best known in this respect are the complexes $[\text{MM}'(\text{CO})_8(\alpha\text{-diimine})]$ ($\text{M}, \text{M}'=\text{Mn}, \text{Re}$) [4–9]. These complexes are usually very photoreactive and, depending on the relative strengths of the metal–metal and metal–CO bonds, homolytic cleav-

age of the metal–metal bond or CO dissociation occurs.

Because of the observed photoreactivity, the lowest-energy absorption band has first been assigned to a $\sigma_b \rightarrow \pi^*$ (α -diimine) transition [4,10,11]. Further studies on this type of complex has led to a different assignment. Raman spectra showed resonance enhancement of intensity for a symmetrical CO stretching vibration, a feature that strongly indicated the presence of metal (d_π) to ligand (π^*) charge transfer (MLCT) transitions [12]. The UV–Vis data confirmed this assignment, since the considerable solvatochromism and high extinction coefficients were not in line with the above assignment to a $\sigma_b \rightarrow \pi^*$ transition. However, since MLCT states themselves are normally not reactive, the photochemistry was proposed to occur by crossing of the MLCT state(s) with a reactive state, most probably the $^3\sigma_b\pi^*$ state [3,8].

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Fig. 1. Schematic structure of the ligands iPr-DAB and iPr-PyCa.

In order to find out if this photolability is a general phenomenon of metal-metal bonded complexes with a lowest-energy MLCT state, we have extended our investigations to complexes of the type $[(\text{CO})_5\text{Mn}-\text{Ru}(\text{Me})(\text{CO})_2(\alpha\text{-diimine})]$. In this article the synthesis, X-ray structure and spectroscopy of two such $[(\text{CO})_5\text{Mn}-\text{Ru}(\text{Me})(\text{CO})_2(\alpha\text{-diimine})]$ ($\alpha\text{-diimine} = N,N'$ -diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB), pyridine-2-carbaldehyde-*N*-isopropylimine (iPr-PyCa)) complexes are described. Only very few complexes are known which contain such a Mn–Ru bond [13,14]. The ligands and complexes are schematically depicted in Fig. 1. From here on the complexes will be denoted as MnRuDAB and MnRuPyCa, in which DAB and PyCa refer to iPr-DAB and iPr-PyCa, respectively.

2. Experimental

2.1. Materials and apparatus

Solvents for synthetic purposes were of reagent grade, dried over sodium wire (tetrahydrofuran (THF), hexane) and freshly distilled under a nitrogen atmosphere. For the spectroscopic studies, solvents of analytical grade (THF, hexane) or UVASOL quality (toluene, CH_2Cl_2) were used, dried over sodium wire (THF, hexane, toluene) or CaCl_2 (acetonitrile (MeCN), CH_2Cl_2) and distilled under a nitrogen atmosphere prior to use. Chemicals for synthetical purposes were purchased and used without further purification. All preparations were performed under a nitrogen atmosphere, using Schlenk techniques. The photoreactive complexes were handled with care under exclusion of light.

IR spectra were recorded on either a Nicolet 7199 B or a BioRad FTS-7 FTIR spectrophotometer. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV-Vis spectrophotometer, equipped with a 3600 data station or a Varian Cary 4E UV-Vis spectrophotometer. Resonance Raman measurements were performed on a Dilor XY spectrometer, using a model SP 2016 argon ion laser as the excitation source, or a model CR 490 tunable dye laser with Rhodamine 6G as the dye. Because of the photoreactivity of the complexes, the sample solution was pumped during the Raman experiment through a home built, air tight flow-

cell, in which the sample was kept under nitrogen. The spectra were corrected for emission of the complexes. ^1H NMR spectra were recorded on a Bruker AC100 or AMX300 spectrometer. Elemental analyses were carried out by the Elemental Analysis Section of the Institute for Applied Chemistry, TNO, Zeist, Netherlands, or by the Microanalytisches Laboratorium of Dornis und Kolbe, Mülheim a. d. Ruhr, Germany.

2.2. Preparations

The ligands *N,N'*-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB) and pyridine-2-carbaldehyde-*N*-isopropylimine (iPr-PyCa) were synthesized by literature methods [15].

The syntheses of the starting compounds for the preparation of the metal-metal bonded complexes, $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(\text{iPr-DAB})]$ and $[\text{Ru}(\text{CF}_3\text{SO}_3)(\text{Me})(\text{CO})_2(\text{iPr-PyCa})]$, have been described in the literature [16]. The $[(\text{CO})_5\text{Mn}-\text{Ru}(\text{Me})(\text{CO})_2(\alpha\text{-diimine})]$ complexes were prepared as follows. To a solution of 1 mmol $[\text{Mn}_2(\text{CO})_{10}]$ in 20 ml THF ~ 0.5 ml sodium-potassium (3:1) alloy was added. The mixture was vigorously stirred for 3 h, after which the complex was completely reduced to $\text{K}[\text{Mn}(\text{CO})_5]$. After removing the excess NaK by filtration, the solution was added to a small excess of the solid $[\text{Ru}(\text{I})(\text{Me})(\text{CO})_2(\text{iPr-DAB})]$ or $[\text{Ru}(\text{CF}_3\text{SO}_3)(\text{Me})(\text{CO})_2(\text{iPr-PyCa})]$ and the mixture was stirred for 3 h in the dark. The solvent was removed by evaporation under vacuum and the complexes were purified by column chromatography on activated silica, using *n*-hexane as eluent. The first, yellow fraction contained $[\text{Mn}_2(\text{CO})_{10}]$. The MnRuDAB complex was obtained in the next, purple fraction. The complex MnRuPyCa was collected using a mixture of hexane/THF in ratio 70/30 as eluent.

MnRuDAB: yield 60%. IR (hexane): 2060 (s), 1999 (s), 1973 (s), 1962 (m), 1949 (m) cm^{-1} . ^1H NMR (CDCl_3): 8.09 (s) (2 imine-CH), 4.40 (m) (2 iPr-CH), 1.31 (d) (6 iPr- CH_3), 1.25 (d) (6 iPr- CH_3), 0.05 (s) (3 CH_3). Anal. Calc. for $\text{C}_{16}\text{H}_{19}\text{MnN}_2\text{O}_7\text{Ru}$: C, 37.88; H, 3.77; N, 5.52. Found: C, 37.76; H, 3.84; N, 5.61%.

MnRuPyCa: yield 50%. IR (hexane): 2046 (s), 2014 (s), 1989 (s), 1960 (m), 1930 (m) cm^{-1} . ^1H NMR (CDCl_3): 8.77 (d) (1 py-H6), 8.53 (s) (1 imine-CH), 7.92 (d) (1 py-H3), 7.81 (t) (1 py-H4), 7.29 (t) (1 py-H5), 4.62 (m) (1 iPr-CH), 1.48 (d) (3 iPr- CH_3), 1.43 (d) (3 iPr- CH_3), 0.08 (s) (3 CH_3). Anal. Calc. for $\text{C}_{17}\text{H}_{15}\text{MnN}_2\text{O}_7\text{Ru}$: C, 37.62; H, 3.93; N, 5.44. Found: C, 37.49; H, 3.31; N, 5.51%.

2.3. Crystal structure determination of $[(\text{CO})_5\text{Mn}-\text{Ru}(\text{Me})(\text{CO})_2(\text{iPr-PyCa})]$

Crystals were grown from a saturated methanol solution at 223 K. Crystal data and numerical details of the structure determination are listed in Table 1.

Table 1
Crystallographic data and refinement details

Formula	C ₁₇ H ₁₅ N ₂ O ₇ MnRu
Molecular weight	515.3
Space group	P2 ₁ /n
a, b, c (Å)	9.6297(7), 20.923(1), 10.166(1)
β (°)	92.190(8)
V (Å ³)	2046.8(3)
Z	4
D _x (g cm ⁻³)	1.67
λ(Cu Kα) (Å)	1.5418
μ(Cu Kα) (cm ⁻¹)	115.4
F(000)	1024
Temperature (K)	293
Final R, R _w	0.035, 0.053
Residual density range (e Å ⁻³)	-0.8 < r.d.r. < +0.7
Observed reflections	3277

A crystal with approximate dimensions 0.25 × 0.30 × 0.50 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation and ω–2θ scan. A total of 3875 unique reflections was measured within the range $-11 \leq h \leq 11$, $-25 \leq k \leq 0$, $-12 \leq l \leq 0$. Of these, 3277 were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin \theta)/\lambda$ was $0.61 \text{ \AA}^{-1}$. Two reference reflections (012, 031) were measured hourly and showed no decrease during the 42 h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $80 < 2\theta < 85^\circ$. Corrections for Lorentz and polarization effects were applied. The positions of Ru and Mn were found by direct methods. The remaining non-hydrogen atoms were found in a subsequent ΔF synthesis. The hydrogen atoms were calculated. Full-matrix least-squares refinement on F , anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to $R=0.035$, $R_w=0.053$, $(\Delta/\sigma)_{\max}=0.61$. A weighting scheme $w=(8.1+F_{\text{obs}}+0.0066F_{\text{obs}}^2)^{-1}$ was used. An empirical absorption correction (DIFABS) [17] was applied, with coefficients in the range 0.75–1.71. The secondary isotropic extinction coefficient [18,19] refined to $G=0.009(5)$. A final difference Fourier revealed a residual electron density between -0.8 and $0.7 \text{ e \AA}^{-3}$. Scattering factors were taken from Cromer and Mann [20]; International Tables for X-ray Crystallography [21]. The anomalous scattering of Ru and Mn was taken into account. All calculations were performed with XTAL [22].

3. Results and discussion

3.1. Crystal structure

The ORTEP drawing of MnRuPyCa is shown in Fig. 2. Table 2 lists the bond lengths and in Table 3 the

Fig. 2. ORTEP drawing of the molecular structure of MnRuPyCa.

Table 2
Selected bond distances (Å) in MnRuPyCa with e.s.d.s in parentheses

Bond	Length	Bond	Length
Ru–Mn	2.9875(8)	Mn–C(14)	1.810(5)
Ru–C(11)	1.867(5)	Mn–C(16)	1.844(6)
Ru–N(1)	2.111(4)	C(11)–O(11)	1.130(7)
Mn–C(13)	1.836(6)	C(12)–O(12)	1.144(6)
Mn–C(15)	1.790(6)	C(13)–O(13)	1.122(8)
Mn–C(17)	1.837(6)	C(14)–O(14)	1.151(6)
Ru–C(10)	2.148(5)	C(15)–O(15)	1.156(7)
Ru–C(12)	1.860(5)	C(16)–O(16)	1.138(7)
Ru–N(2)	2.099(3)	C(17)–O(17)	1.149(8)

bond angles are summarized. The two metal fragments are bonded to each other by a metal–metal bond. In this dinuclear complex both the $\text{Mn}(\text{CO})_5^-$ and the $\text{Ru}(\text{Me})(\text{CO})_2(\text{iPr-PyCa})$ moieties possess an 18-electron configuration and a slightly distorted octahedral geometry. The CO ligands of $\text{Mn}(\text{CO})_5$ and $\text{Ru}(\text{Me})(\text{CO})_2(\text{iPr-PyCa})$ are in staggered positions, just as for $[\text{Mn}_2(\text{CO})_{10}]$ [23] and $[\text{Ru}(\text{Me})(\text{CO})_2(\text{iPr-DAB})]_2$ [24].

Only a few dinuclear complexes with a manganese–ruthenium bond are known. For the complex $[\text{RuMn}(\text{CO})_8(\text{R}-\text{C}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N-iPr})]$ ($\text{R}=\text{Ph}$, Me), the presence of a metal–metal bond has been proposed, but this was not confirmed by an X-ray crystal structure determination [13]. The manganese–ruthenium bond in $[(\text{CO})_4\text{Mn}(\mu\text{-H})(\mu\text{-PPh}_2)-\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]$ [14] ($2.894(1) \text{ \AA}$) is considerably shorter than in MnRuPyCa ($2.9875(8) \text{ \AA}$). This is most probably caused by the presence of bridging ligands. This bond is also longer than that found for the Mn–Mn bond in $[\text{Mn}_2(\text{CO})_{10}]$ ($2.9038(6) \text{ \AA}$ [23]) and the Ru–Ru bond in $[\text{Ru}(\text{Me})(\text{CO})_2(\text{iPr-DAB})]_2$ ($2.940(1) \text{ \AA}$) [24].

Table 3
Selected angles (°) in MnRuPyCa with e.s.d.s in parentheses

Bond	Angle	Bond	Angle	Bond	Angle
Mn–Ru–C(10)	175.6(2)	Mn–Ru–C(11)	86.9(2)	C(13)–Mn–C(14)	91.0(2)
Mn–Ru–C(12)	90.8(2)	Mn–Ru–N(1)	94.9(1)	C(13)–Mn–C(16)	167.4(3)
Mn–Ru–N(2)	95.38(9)	C(10)–Ru–C(11)	89.0(2)	C(14)–Mn–C(15)	96.8(2)
C(10)–Ru–C(12)	90.7(2)	C(10)–Ru–N(1)	84.0(2)	C(14)–Mn–C(17)	164.8(2)
C(10)–Ru–N(2)	88.6(2)	C(11)–Ru–C(12)	88.7(2)	C(15)–Mn–C(17)	98.4(3)
C(11)–Ru–N(1)	97.0(2)	C(11)–Ru–N(2)	174.0(2)	C(13)–Mn–C(15)	94.4(2)
C(12)–Ru–N(1)	172.2(2)	C(12)–Ru–N(2)	96.9(2)	C(13)–Mn–C(17)	88.8(3)
N(1)–Ru–N(2)	77.2(1)	Ru–Mn–C(13)	83.8(2)	C(14)–Mn–C(16)	87.6(2)
Ru–Mn–C(14)	79.1(1)	Ru–Mn–C(15)	175.5(2)	C(15)–Mn–C(16)	98.2(3)
Ru–Mn–C(16)	83.6(2)	Ru–Mn–C(17)	85.7(2)	Mn–C(13)–O(13)	176.4(5)
Ru–C(12)–O(12)	177.4(5)	Mn–C(16)–O(16)	178.0(5)	Mn–C(15)–O(15)	178.0(5)
Mn–C(14)–O(14)	177.0(4)	Ru–C(11)–O(11)	177.5(6)	Mn–C(17)–O(17)	179.1(6)

The iPr-PyCa ligand coordinates via $\sigma(N1)$ and $\sigma(N2)$ to the ruthenium centre, which is similar to the $[(CO)_5Re-Mn(CO)_3(iPr-DAB)]$ and $[Ph_3Sn-Mn(CO)_3-(tBu-DAB)]$ complexes [25]. The bite angle of $77.2(1)^\circ$, which causes the deviation from a regular octahedral structure, is also found in $[Ru(I)(C(O)Me)(CO)_2(iPr-DAB)]$ [26] and in the dinuclear complex $[Ru(Me)(CO)_2(iPr-DAB)]_2$ [24].

The Ru–Me bond of $2.148(5)$ Å is comparable with the $2.152(5)$ Å bond length in $[Ru(Me)(CO)_2(iPr-DAB)]_2$ [24]. These distances are somewhat larger than found for $[Ru(I)(C(O)Me)(CO)_2(iPr-DAB)]$ ($2.0788(8)$ Å) [26] and $[Ru(CF_3SO_3)(Me)(CO)_2(iPr-DAB)]$ ($2.122(10)$ Å) [26] due to the larger *trans* effects of the $Mn(CO)_5$ and Me groups with respect to I^- and $CF_3SO_3^-$. The Ru–CO bonds ($\sim 1.863(5)$ Å) are slightly longer than in these mononuclear complexes ($1.840(9)$ Å), but comparable with the $1.867(5)$ Å Ru–CO bonds in $[Ru(Me)(CO)_2(iPr-DAB)]_2$ [24].

3.2. UV-Vis spectra

The UV-Vis spectra of the complexes MnRuDAB and MnRuPyCa are dominated by an intense band in the visible region. This band is characterized by high extinction coefficients (MnRuDAB: $\epsilon = 13\,000\text{ M}^{-1}\text{ cm}^{-1}$ in THF; MnRuPyCa: $\epsilon = 9000\text{ M}^{-1}\text{ cm}^{-1}$ in THF). In addition to this band, a strongly allowed electronic transition is found near 310 nm.

Table 4 and Fig. 3(a) show a considerable solvent dependence of the lowest energy absorption band. For MnRuDAB, a 30 nm red shift is observed going from MeCN to hexane; MnRuPyCa shows an even larger shift of 68 nm. These solvent shifts are characteristic for charge transfer transitions [27]. Thus, the d^6 complexes $[M(CO)_4(\alpha\text{-diimine})]$ ($M = Cr, Mo, W$) experience a similar, large influence of the solvent polarity and also show that the solvatochromic shift is smaller for complexes with the larger π -acceptor capability of the α -diimine ligand. The latter effect is due to an

Table 4
Solvatochromism of MnRuDAB and MnRuPyCa at room temperature ($\lambda_{\max, \text{abs}}$ in nm)

Solvent	$\lambda_{\max, \text{abs}}$	
	MnRuDAB	MnRuPyCa
Acetonitrile	311, 549	316, 541
THF	312, 558	317, 556
Toluene	310, 570	318, 585
Hexane	312, 579	313, 609

increased mixing between the metal- d_π and α -diimine- π^* orbitals when they become closer in energy. This is the case when iPr-PyCa is replaced by iPr-DAB. The CT transition is then accompanied with a smaller change in dipole moment and, as a result, the electronic transition will be less dependent on the solvent polarity in the case of MnRuDAB.

The other absorption band near 310 nm is not solvent dependent. A similar band found for $[Mn_2(CO)_{10}]$ was assigned to the $\sigma_b \rightarrow \sigma^*$ transition. Another characteristic property of this band is that it sharpens up at low temperature without shifting to higher energy. This is illustrated in Fig. 3(b) in which the absorption spectra of MnRuPyCa are presented at room temperature and at 77 K.

3.3. Resonance Raman spectra

In order to confirm the assignment of the lowest energy transitions, resonance Raman (rR) spectra of the two complexes have been measured by excitation into these transitions. This rR technique has proven to be very valuable since Raman bands belonging to vibrations, which are coupled to an allowed electronic transition, will be enhanced in intensity when excitation takes place into this transition. Unfortunately, the complexes were too photolabile for normal Raman measurements in a standard cuvette, KNO_3 disk or even

Fig. 3. UV-Vis absorption spectra of MnRuPyCa in hexane, THF and acetonitrile (top) and of the same complex in 2-Cl-butane at r.t. and 77 K (bottom).

Fig. 4. Resonance Raman spectra of (a) MnRuDAB ($\lambda_{\text{exc}} = 532$ nm) and (b) MnRuPyCa ($\lambda_{\text{exc}} = 514.5$ nm) in CH_2Cl_2 at r.t. Solvent bands are indicated with an asterisk.

a spinning cell. Therefore, a special flow-through cell was constructed, which could be handled under a nitrogen atmosphere.

Representative spectra of the two complexes are shown in Fig. 4. Fig. 5 presents the wavelength dependence of the Raman intensity in a so-called 'excitation profile' for the two vibrations of the MnRuPyCa complex.

For MnRuDAB the strongest rR effect is observed for $\nu_s(\text{CN})$ of the iPr-DAB ligand at 1485 cm^{-1} . This means that the electronic transition is indeed accompanied by transfer of negative charge to this ligand. The value of 1485 cm^{-1} is much lower than that

Fig. 5. Resonance Raman excitation profiles of $\nu_s(\text{CO})$ and $\nu_s(\text{CN})$ (at 1573 cm^{-1}) of MnRuPyCa.

measured for a mononuclear halide complex such as $[\text{Ru}(\text{Cl})(\text{Me})(\text{CO})_2(\text{iPr-DAB})]$ ($\nu_s(\text{CN}) = 1568\text{ cm}^{-1}$) [28]. This effect is caused by the stronger electron-donating properties of the $\text{Mn}(\text{CO})_5$ group with respect to Cl, which is reflected in an increase of π -backdonation to the iPr-DAB ligand. The difference in electron-donating character between $\text{M}(\text{CO})_5$ and Cl is also reflected in the absorption spectra, since the lowest energy transitions shift from 435 to 558 nm when Cl is replaced by $\text{M}(\text{CO})_5$.

The complex MnRuPyCa has more Raman bands between 1400 and 1700 cm^{-1} (1472 , 1573 and 1610 cm^{-1}) which belong to symmetrical stretching modes of the imine group and pyridine ring.

The deformation modes of the iPr-DAB (833 , 951 cm^{-1}) and iPr-PyCa (972 , 1023 cm^{-1}) compounds are more intense than for the corresponding halide complexes. This again illustrates the stronger mixing between the metal- d_π and α -diimine- π^* orbitals for the complexes under study with respect to the halide complexes. For, an increase of mixing decreases the charge transfer character of the electronic transition which then becomes more metal-ligand bonding to antibonding. The complex will distort in this metal-ligand antibonding (π^*-d_π) excited state and this distortion is reflected in the rR effects for the deformation modes of the α -diimine ligand. A similar effect has been observed for the metal-metal bonded complexes $[(\text{CO})_5\text{M}-\text{M}'(\text{CO})_3(\alpha\text{-diimine})]$ ($\text{M}, \text{M}' = \text{Mn}, \text{Re}$) [7].

In accordance with the complexes $[\text{Mn}_2(\text{CO})_{10}]$, $[\text{Re}_2(\text{CO})_{10}]$ and $[(\text{CO})_5\text{M}-\text{M}'(\text{CO})_3(\alpha\text{-diimine})]$ ($\text{M}, \text{M}' = \text{Mn}, \text{Re}$) [7,29], $\nu_s(\text{Mn-Ru})$ is expected in the frequency region 100 – 250 cm^{-1} . The rR spectra did not show any strong band in this region which means that the metal-metal bond is hardly affected by the electronic transitions in the visible region.

Finally, the complexes show an rR effect for a $\nu_s(\text{CO})$ Raman band at 2048 (MnRuPyCa) and 2056 (MnRuDAB) cm^{-1} , respectively. The frequencies of these bands are high compared to the values obtained for related complexes. Thus, the highest $\nu_s(\text{CO})$ frequency

of $[\text{Ru}(\text{Cl})(\text{Me})(\text{CO})_2(\text{iPr-DAB})]$ is at 2033 cm^{-1} (CH_2Cl_2) [28]. As shown before, replacement of Cl by $\text{Mn}(\text{CO})_5$ increases the electron density at Ru and the π -backbonding to the iPr-DAB ligand. At the same time, π -backbonding to the CO ligands will also increase and the frequency of $\nu_s(\text{CO})$ is expected to decrease instead of to increase. The observed discrepancy is attributed to a coupling of the CO vibrations of the $\text{Ru}(\text{Me})(\text{CO})_2(\alpha\text{-diimine})$ moiety with those of the $\text{Mn}(\text{CO})_5$ fragment. For, if Cl in $[\text{Ru}(\text{Cl})(\text{Me})(\text{CO})_2(\text{iPr-DAB})]$ is replaced by the strongly electron-donating SnPh_3 group to give $[\text{Ru}(\text{SnPh}_3)(\text{Me})(\text{CO})_2(\text{iPr-DAB})]$, the frequency of $\nu_s(\text{CO})$ is lowered from 2024 (THF) to 2003 cm^{-1} [30], according to expectations. A similar effect is observed when both Me and Cl are replaced by SnPh_3 groups to give $[\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(\text{iPr-DAB})]$ [30]. The frequency of $\nu_s(\text{CO})$ is then lowered from 2024 to 2005 cm^{-1} . On the other hand, substitution of Cl by $\text{Mn}(\text{CO})_5$ or $\text{Co}(\text{CO})_4$, as well as substitution of Cl by $\text{Mn}(\text{CO})_5$ or $\text{Co}(\text{CO})_4$ and Me by SnPh_3 , always gives rise to a frequency increase of $\nu_s(\text{CO})$, although at the same time the electron density at the Ru centre increases since the first absorption band shifts from 435 to 515–560 nm [30]. Based on these observations, the highest frequency observed in the rR spectra of the complexes under study, is assigned to a coupled vibration of both metal fragments.

The excitation profiles of Fig. 5 demonstrate that the first absorption band consists of only one strongly allowed electronic transition to which both $\nu_s(\text{CN})$ of the α -diimine and $\nu_s(\text{CO})$ are coupled. Apparently, the second transition, observed as a shoulder in the low-temperature spectrum of MnRuPyCa (Fig. 3(b)), does not contribute to the rR intensity. These rR effects point to oxidation of the metal and reduction of the α -diimine. The electronic transition will therefore be metal-to- α -diimine charge transfer (MLCT) in character. The transition originates from a Ru-d_π orbital and not from $\sigma_b(\text{Mn-Ru})$. For, excitation from Ru-d_π will decrease the metal-to-CO π -backbonding and be responsible for the rR effect of $\nu_s(\text{CO})$, whereas excitation from $\sigma_b(\text{Mn-Ru})$ would have been accompanied with a strong rR effect for $\nu_s(\text{Mn-Ru})$.

This result is of importance for the interpretation of the photochemistry of these complexes [31]. The main issue is that, as mentioned in Section 1, all metal-metal bonded carbonyls containing an α -diimine ligand are highly photoreactive, although visible excitation leads to occupation of non-reactive MLCT states. The above results show that the complexes MnRuDAB and MnRuPyCa also have low-energy MLCT ($\text{d}_\pi\pi^*$) states. The homolytic splitting of the Mn–Ru bond, observed for these complexes [31], must therefore proceed from a state, presumably $^3\sigma_b\pi^*$, which is not directly occupied by visible excitation but only indirectly via non-reactive MLCT states. Although the absorption

and rR spectra clearly show that the $\sigma_b \rightarrow \pi^*$ transition does not contribute to the visible absorption band, the presence of a $^3\sigma_b\pi^*$ state at rather low energy has recently been established for these complexes by a weak and long lived emission in an MeTHF glass at 77 K [32]. The consequences of these absorption, rR and emission data for the photochemical behaviour of these complexes will be discussed in a forthcoming article [31].

4. Conclusions

The $[(\text{CO})_5\text{Mn-Ru}(\text{Me})(\text{CO})_2(\alpha\text{-diimine})]$ complexes under study have an uncommon Mn–Ru bond as evidenced by a crystal structure determination. The absorption bands are assigned with the use of rR spectroscopy to MLCT transitions, which cannot be responsible for the observed photochemistry.

5. Supplementary material

Listings of the atomic coordinates of non-hydrogen (Table S1) and hydrogen (Table S2) atoms, the anisotropic thermal parameters of the non-hydrogen atoms (Table S3), the non-essential bond lengths of the non-hydrogen atoms (Table S4) and hydrogen atoms (Table S5), and the non-essential bond angles of the non-hydrogen atoms (Table S6) and hydrogen bond angles (Table S7), and of structure factor amplitudes (25 pages) are available from the authors on request.

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