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Monomeric and dimeric Re(I)(tricarbonyl)(8-quinolinato) complexes

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A simple synthetic procedure (reaction between $Re(CO)_5Cl$ and 8-hydroxyquinoline, HOX, in boiling toluene) leads to the dimeric complex $Re_2(CO)_6(OX)_2$. In coordinating solvents $Re_2(CO)_6(OX)_2$ undergoes dissociative solvolysis (*via* a second order reaction) to form monomeric species of general formula $Re(CO)_3(OX)$solv. In non-coordinating media, however, the dimeric complex remains unaffected. Molecular structures of both forms (which are in accord with IR absorption spectra) were confirmed by means of X-ray measurements. UV-VIS spectroscopic (absorption and emission) properties of both newly synthesized Re(I) complexes have been investigated and the differences in their luminescence properties have been briefly discussed.

Introduction

Understanding the relationship between the structure of transition metal complexes and their photophysical and photochemical properties[1–4] is one of the most important tasks in inorganic physical chemistry. Besides the theoretical points of interest connected with the presence of a panoply of electronic excited-states for such complexes, studies on their properties have received additional momentum since they have been considered to be potentially useful in numerous practical applications. Typical examples involve optical, chemiluminescent and electroluminescent sensors,[5–8] molecular wires and switches,[9–12] photocatalysis[13–16] and probes of the structural features of polymers.[17,18]

In recent decades the diimine chelates (*e.g.*, 2,2′-bipyridine, 1,10-phenanthroline and their derivatives) of d^6 metals have attracted increasing interest with special attention paid to complexes containing the $Re(CO)_3^+$ fragment and a remarkable amount of work has been devoted towards the characterisation of their luminescent properties[19–23] (essential for some of the above mentioned applications).

In the pseudooctahedral Re(I) carbonyl complexes emission of light mainly originates from the metal-to-ligand charge-transfer (MLCT) excited state, but the influence of the energetically higher intraligand (IL) excited states has been reported.[24,25] In particular cases, even subtle ligand modification can be sufficient to cause a significant change in the electronic structure of the emitting state. However, due to small energy differences between neighbouring states, in some cases a precise assignment of the lowest excited electronic level may be difficult, *e.g.*, because of mixing of the lowest excited state with other close-lying states of higher energy.[26,27] The MLCT character of the lowest, luminescent excited state in the $Re(CO)_3^+$ complexes arises from the relatively low energy of the ligand π^* orbitals. It is expected that replacement of the ligand with another one having π^* orbitals of rather high energy should prevent low-energy electronic excitations to cause the MLCT transition and, by the same token, change the nature of the lowest excited state to the IL type. Recently, the 8-quinolinolate anion has been proposed as a suitable bidentate ligand for investigation of the still largely unexplored type of IL transitions in the Re(I) carbonyl complexes.[28] The easy synthetic route, namely, boiling of equimolar amounts of $Re(CO)_5Cl$ and 8-hydroxyquinoline (HOX) in toluene, leads to a reaction product with the proposed formula (on the basis of elemental analysis only) $Re(CO)_4(OX)$.

$$Re(CO)_5Cl + HOX \longrightarrow Re(CO)_4(OX) + HCl + CO \quad (1)$$

The obtained complex exhibits two emission bands in acetonitrile (ACN) solutions, “green” and “red”, respectively. The observation of the dual emission is consistent with luminescence studies on other 8-quinolinolate complexes.[29–31]

Taking into account the reported[28] “strongly” emissive properties of this compound and considering its use as a material for our further electroluminescence[32,33] and electrochemiluminescence[34,35] studies, we decided to repeat the synthesis and to investigate the luminescent properties of the product in detail. Following the described procedure[28] we obtained a product with UV-VIS spectroscopic properties in agreement with those previously reported. However, the preliminary electron impact mass spectrometry (EIMS) results have not exactly agreed with the proposed $Re(CO)_4(OX)$ formula. It has been found that the most intense peaks correspond to the mass/charge ratio characteristic for the $Re(CO)_3(OX)^+$, $Re(CO)_2(OX)^+$, $Re(CO)(OX)^+$ and $Re(OX)^+$ fragments. Surprisingly the recorded mass spectrum did not show any signal expected for the $Re(CO)_4(OX)^+$ ion. Contrary to this, the MS results have suggested the molecular weight to be as high as 828–830, probably corresponding to a molecular formula such as $Re_2(CO)_6(OX)_2$ (natural abundance of ^{185}Re and ^{187}Re isotopes is 37 and 63%, respectively). Moreover, crystallisation of the crude reaction product from different solvents has resulted in species displaying distinctly different IR and UV-VIS spectroscopic properties. These facts have indicated that reaction (1) and the final product formula (as proposed in ref. 28) might not be correct. A more detailed study on the product of the reaction between $Re(CO)_5Cl$ and 8-hydroxyquinoline was the aim of the present work.

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Table 1 Crystal data and structure refinement for $Re_2(CO)_6(OX)_2$ and $Re(CO)_3(OX)pyr$ molecules

	$Re_2(CO)_6(OX)_2$	$Re(CO)_3(OX)pyr$
Chemical formula	$C_{24}H_{12}N_2O_8Re_2$	$C_{17}H_{11}N_2O_4Re$
Formula weight	829.97	493.48
Crystal system	Orthorhombic	Triclinic
a/Å	9.785(2)	7.089(1)
b/Å	14.327(3)	9.418(2)
c/Å	16.454(3)	12.493(2)
α/°		87.77(3)
β/°		82.66(3)
γ/°		75.20(3)
Unit-cell volume/$Å^3$	2306.7(8)	799.8(2)
T/K	293(2)	293(2)
Space group	$P2(1)2(1)2(1)$	P-1
Z	4	2
Linear absorption coefficient/mm^{-1}	10.540	7.620
Absorption correction	Numerical	Numerical
Max. and min. transmission	0.6476 and 0.3151	0.2189 and 0.0679
Data/restraints/parameters	5546/0/337	3884/0/229
R indices (all data)	0.0403; $wR(F^2) = 0.0826$	0.0248; $wR(F^2) = 0.0595$
Final R indices [$I > 2\sigma(I)$]	0.0546; $wR(F^2) = 0.0917$	0.0277; $wR(F^2) = 0.0622$

Experimental

Materials

Butyronitrile (Merck, for synthesis) was triply distilled over $KMnO_4 + K_2CO_3$, P_2O_5, and CaH_2, successively. All other solvents used for our studies were of spectroscopic grade (Aldrich or Merck). Solutions for the emission measurements were deaerated by saturation with argon.

Syntheses

$Re_2(CO)_6(OX)_2$. Was obtained (in almost quantitative yield) by reacting an equimolar suspension of $Re(CO)_5Cl$ (Strem Chemicals) and 8-hydroxyquinoline (Polish Chemicals) in refluxing toluene under argon for about 3 hours. After cooling to room temperature the reaction mixture was condensed by evaporation of toluene under vacuum. After slow evaporation of the remaining solvent yellow crystals precipitated. The crude product was recrystallised from a toluene–dichloromethane mixture (Found: C, 35.45; H, 1.54; N, 3.45. $C_{24}H_{12}N_2O_8Re_2$ requires C, 34.70; H, 1.46; N, 3.37%).

$Re(CO)_3(OX)pyr$. Was obtained as orange crystals in quantitative yield by dissolving $Re_2(CO)_6(OX)_2$ in pyridine (pyr) and subsequent slow evaporation of the excess solvent (Found: C, 41.37; H, 1.80; N, 5.64. $C_{17}H_{11}N_2O_4Re$ requires C, 41.29; H, 2.24; N, 5.67%).

Experimental techniques

IR and UV-VIS absorption were measured by means of a Perkin-Elmer Spectrum 2000 FT-IR and Shimadzu UV 2401 PC spectrophotometers, respectively. Fluorescence spectra (corrected for the spectral sensitivity of the instrument) were recorded using an Edinburgh Instruments FS900 steady-state fluorimeter. As a quantum yield standard a solution of quinine sulfate in 0.1 N H_2SO_4 ($\Phi_f = 0.51$)[36] was used. Low-temperature (77 K) luminescence spectra were recorded in butyronitrile (BN) glasses by means of a Jasny spectrofluorimeter.[37]

Fresh (prepared just before each experiment) solutions of $Re_2(CO)_6(OX)_2$ in dichloromethane (DCM) were used in the solvolysis kinetic studies. Into 3 ml of this solution (in the absorption cell) a known volume (5–100 µl, corresponding to a concentration within the range 0.02–0.5 M) of a solvolysing agent was added. The absorption at 440 nm was recorded every 100 seconds and the resulting solvolysis rate constants have been determined within an estimated error of 15–20%.

Crystal structure data for dimeric $Re_2(CO)_6(OX)_2$ and monomeric $Re(CO)_3(OX)pyr$ are given in Table 1, together with refinement details. X-Ray measurements were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal was positioned at 62 mm from the KM4CCD camera. 256 frames were measured at 1.3° intervals with a counting time of 15 s for the dimeric complex. Correspondingly 748 frames at 1.2° intervals with a counting time of 25 s were applied for the monomeric complex. The data were corrected for Lorentz and polarisation effects and numerical absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs. The structures were solved by direct methods[38] and refined using SHELXL.[39] The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_o^2 > 2s(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. All hydrogen atoms were located from a difference map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in ref. 40.

CCDC reference numbers 158606 and 158607.

See http://www.rsc.org/suppdata/dt/b1/b101357m/ for crystallographic data in CIF or other electronic format.

Results and discussion

Molecular structures

As the elemental analysis did not provide a definitive chemical identification of the studied complexes and taking into account the preliminary results from the mass spectrometry investigation we decided to carry out X-ray diffraction measurements as the decisive proof. The ORTEP[41] schemes for both investigated complexes are presented in Fig. 1.

It has been revealed that molecules of the compound obtained directly from the reaction of $Re(CO)_5Cl$ with HOX have a dimeric form, with two $Re(CO)_3(OX)$ subunits merged by two bridging 8-quinolinato oxygen atoms. Heterocyclic rings of the OX ligands lie on the same side of a virtual surface containing rhenium, the oxygen atoms and two pairs of carbonyl groups, almost perpendicular to the surface and set antiparallel to each other. The nitrogen containing ring of one ligand faces the phenolic side of the second one. The Re–O bonds are not the same length (1.165 and 2.204 Å) indicating ionic and covalent character of the given bonds, respectively. Each $Re(CO)_3^+$ core is bound more strongly by the oxygen atom belonging to the OX anion within the $Re(CO)_3(OX)$

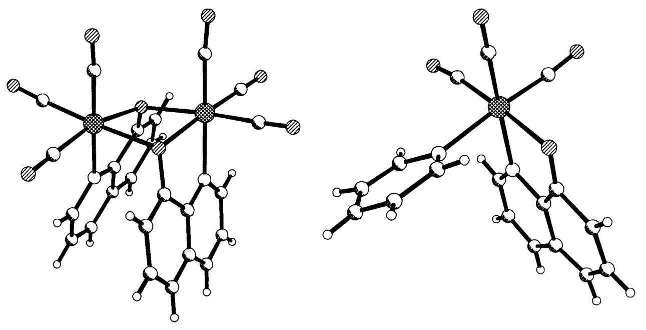

Fig. 1 ORTEP schemes of $Re_2(CO)_6(OX)_2$ (left) and $Re(CO)_3(OX)pyr$ (right) molecules.

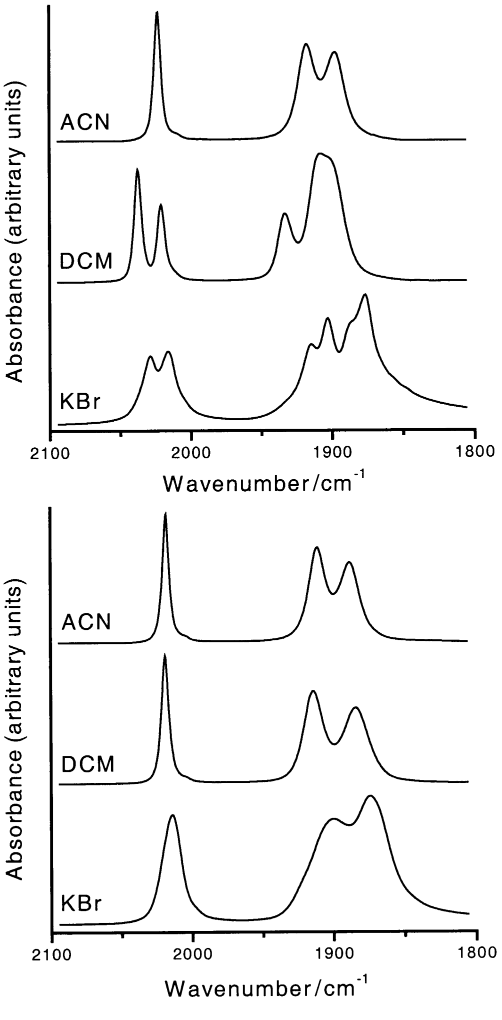

Fig. 2 IR spectra (the carbonyl CO stretching region) of $Re_2(CO)_6(OX)_2$ (top) and $Re(CO)_3(OX)pyr$ (bottom) molecules in a KBr matrix and dichloromethane (DCM) or acetonitrile (ACN) solutions.

subunit. It should be noted that the $Re(CO)_3(OX)$ cores are not exactly identical, *i.e.* the lengths of corresponding bonds (especially for Re–C and carbonyl C–O) are slightly (*ca.* 0.01 Å) different. This is nicely reflected in the IR spectra, particularly in the spectral region corresponding to the carbonyl stretching vibrations (ν_{CO}) from 1700–2100 cm^{-1}. Pseudooctahedral Re(I) complexes with three facial CO ligands, usually display three bands in this region.[42] In the case of dimeric $Re_2(CO)_6(OX)_2$ one could expect that these bands would be split due to the small differences in the appropriate bond lengths. In fact, in KBr, such splitting is observed (*cf.* Fig. 2).

Recrystallisation of $Re_2(CO)_6(OX)_2$ from pyridine results in another Re(I) complex (*cf.* Fig. 1). The obtained molecule $Re(CO)_3(OX)pyr$ is monomeric and contains a pyridine coord-

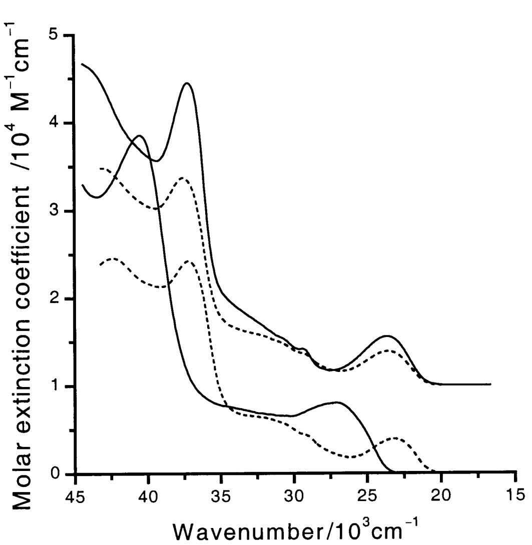

Fig. 3 Room temperature UV-VIS absorption spectra of $Re_2(CO)_6(OX)_2$ (solid lines) and $Re(CO)_3(OX)pyr$ (dashed lines) in dichloromethane (DCM) or acetonitrile (ACN) solutions. The spectra in ACN solutions are shifted along the *y*-axis (by a factor 1×10^4 M^{-1} cm^{-1}). In ACN solutions the dissociative solvolysis of the dimeric $Re_2(CO)_6(OX)_2$ leads to the monomeric $Re(CO)_3(OX)ACN$ complex (see text).

inated *via* its N atom to the $Re(CO)_3^+$ core, nearly perpendicular to the surface of the 8-quinolinato ring system. On the basis of the bond lengths the covalent character of Re–N bonds in both studied complexes may be proposed (*cf.* refs. 29–31). The monomeric structure of $Re(CO)_3(OX)pyr$ agrees well with the results of IR spectroscopic studies. As expected, three distinct ν_{CO} bands can be observed. The distinct features of the IR spectra of both monomeric and dimeric forms can also be used as fingerprints of species existing in solution (*vide infra*).

UV-VIS absorption and luminescence

Both complexes, $Re_2(CO)_6(OX)_2$ and $Re(CO)_3(OX)pyr$, are soluble in a wide range of solvents, polar and less polar as well. Differences between the two are manifested particularly in the electronic absorption and emission properties. The UV-VIS absorption spectra of $Re(CO)_3(OX)pyr$ are nearly independent of solvent (*cf.* Fig. 3). In the low energy region it shows one band at 420–430 nm ($\varepsilon \approx 3900$ M^{-1} cm^{-1}). The second band of similar intensity, which occurs as a shoulder at ≈325 nm, is partially obscured by another band of higher energy. In the short wavelength region two bands at 266 and 232 nm (with similar extinction coefficients $\varepsilon \approx 2.4 \times 10^4$ M^{-1} cm^{-1}) are displayed. $Re(CO)_3(OX)pyr$ is luminescent in all studied solutions displaying both the "red" and the "green" emission (*cf.* Fig. 4). The spectral positions of both the short and long wavelength luminescence are almost independent of solvent. The quantum efficiency of the first emission is only $\approx 1 \times 10^{-4}$ in all studied media; the second emission is several times higher being about $1\text{–}4 \times 10^{-3}$. In analogy to other 8-quinolinato transition metal complexes (*e.g.*, Pb, Bi 8-quinolato chelates)[29–31] the "red" emission (maximum intensity at 14500–15000 cm^{-1}) is completely quenched in air-saturated samples, whereas the intensity of the "green" emission (at ≈19000 cm^{-1}) is only slightly affected.

The absorption and luminescent properties of $Re_2(CO)_6(OX)_2$ in a series of strongly coordinating solvents (like pyridine, esters, nitriles or amides, characterised by relatively high values of the donor number DN,[43,44] *i.e.* a parameter characterising the solvent donicity) resemble the properties of $Re(CO)_3(OX)pyr$ quite well (*cf.* Figs. 3 and 4). However, in weakly coordinating solvents like DCM (DN ≈ 0), its spectroscopic characteristic is substantially different. This dissimilarity is manifested by the lack of absorption of light at wavelengths longer than ≈420 nm and the lack of phosphorescence. Unlike

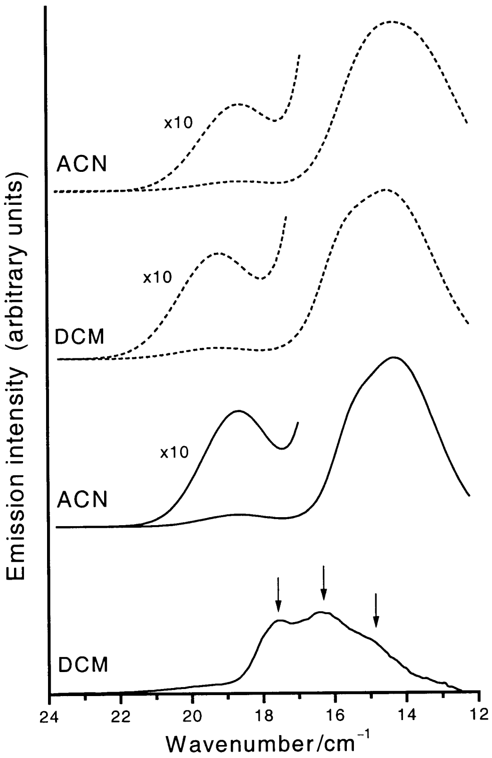

Fig. 4 Room temperature luminescence spectra of $Re_2(CO)_6(OX)_2$ (solid lines) and $Re(CO)_3(OX)pyr$ (dashed lines) in dichloromethane (DCM) or acetonitrile (ACN) solutions.

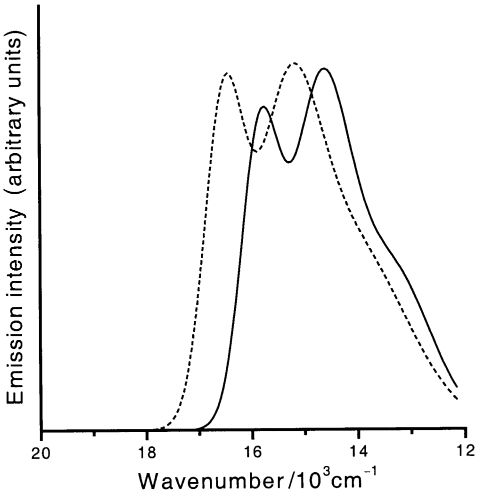

Fig. 5 Phosphorescence spectra (in butyronitrile, BN, glasses at 77 K) of $Re(CO)_3(OX)pyr$ (solid line) and $Re(CO)_3(OX)BN$ (dashed line). In BN solutions the dissociative solvolysis of the dimeric $Re_2(CO)_6(OX)_2$ leads to the monomeric $Re(CO)_3(OX)BN$ complex (see text).

in the cases of $Re(CO)_3(OX)pyr$ solutions or $Re_2(CO)_6(OX)_2$ itself in the rest of the solvents, the fluorescence band in DCM is structured and displays two distinct peaks at 16500 and 17500 cm^{-1}. Oxygen saturation of a probe does not change distinctly the fluorescence quantum efficiency.

Addition of small amounts of strongly coordinating solvents to a solution of $Re_2(CO)_6(OX)_2$ in DCM changes the spectroscopic properties of the solute to that characteristic for $Re(CO)_3(OX)pyr$. The solution probably contains only the monomeric complex formed as a result of the dissociative solvolysis of $Re_2(CO)_6(OX)_2$. Most probably, their formulae can be written as $Re(CO)_3(OX)solv$, where solv represents a molecule of solvent bearing an electron-rich group (*e.g.*, CN, CO), that enables coordination to the metal centre.

$$Re_2(CO)_6(OX)_2 + 2solv \longrightarrow 2Re(CO)_3(OX)solv \quad (2)$$

The above conclusion is in good agreement with the results of IR spectroscopic studies. The existence of a monomeric form of the studied complexes in solutions can be proven by IR absorption measurements (*cf.* Fig. 2). IR spectra of $Re(CO)_3(OX)pyr$ in ACN as well as in DCM are very similar to that measured in KBr. In contrast, the IR spectrum of $Re_2(CO)_6(OX)_2$ in ACN solution looks very similar to that for $Re(CO)_3(OX)pyr$, instead of showing the splitting of the ν_{CO} bands, characteristic for the dimeric form observed in KBr. However, the IR spectrum of dimeric $Re_2(CO)_6(OX)_2$ in DCM solution exhibits splitting of its carbonyl CO bands similarly to the spectrum in KBr. Hence, non-coordinating solvents are not able to solvolyse the dimeric complex and in such media it remains unaffected.

Similarities in the spectroscopic behaviour of the $Re_2(CO)_6(OX)_2$ solvolysis product to that of $Re(CO)_3(OX)pyr$, which is one of the members of the homologous series $Re(CO)_3(OX)solv$ would thus be connected with similarities in their structures. IR spectra (recorded for $Re_2(CO)_6(OX)_2$ and $Re(CO)_3(OX)pyr$ in ACN solutions) suggest also that solubilisation of $Re(CO)_3(OX)pyr$ in ACN does not lead to replacement of coordinated pyr ligand by a solvent molecule. Low-temperature phosphorescence spectra (Fig. 5) of both complexes $Re(CO)_3(OX)pyr$ and $Re_2(CO)_6(OX)_2$ in BN glasses support the above conclusion. A comparison of the phosphorescence bands of the two complexes: $Re(CO)_3(OX)pyr$ and $Re(CO)_3(OX)BN$ (the presumable product of the reaction of $Re_2(CO)_6(OX)_2$ with BN) reveals that the shapes of the bands are similar (two distinct branches spaced by ≈1200 cm^{-1}), but the position of the $Re(CO)_3(OX)pyr$ emission is red-shifted by about 800 cm^{-1}. It may suggest some contribution of MLCT character to the observed phosphorescence ($Re(CO)_3pyr^+$ fragment seems to be a better electron donor in comparison to $Re(CO)_3BN^+$).

$Re_2(CO)_6(OX)_2$ solvolysis

In view of the UV-VIS absorption data one can conclude that dissociation of $Re_2(CO)_6(OX)_2$ into $Re(CO)_3(OX)solv$ occurs in most of the solvents studied (only in poorly donating ones, *e.g.*, DCM with DN ≈ 0 is $Re_2(CO)_6(OX)_2$ stable). In such media as BN, dimethylsulfoxide (DMSO) or *N*,*N*-dimethylformamide (DMF) the solvolysis is extremely rapid (too fast to be measurable using our equipment) and is complete immediately upon preparation of the solutions. This seems to be a general rule in solvents with high values of DN. In a similar way, addition of small amounts of strongly coordinating solvent to a DCM solution of $Re_2(CO)_6(OX)_2$ changes the spectroscopic properties of the solute to that characteristic for $Re(CO)_3(OX)pyr$. The process is much slower than in pure solvents and it has been possible to record composition evolution of solutions prepared by introduction of known amounts of a coordinating agent (*e.g.*, pyridine) into DCM solutions of $Re_2(CO)_6(OX)_2$. It has allowed us to evaluate some kinetic parameters (reaction order, rate constants). The control of reaction progress was possible due to the fact that the dimeric complex $Re_2(CO)_6(OX)_2$ is practically transparent at wavelengths longer than 420 nm, whereas the monomeric complexes (products of reaction (2)) show intense absorption. A typical example of the time evolution of the UV-VIS absorption spectra for the $Re_2(CO)_6(OX)_2$–pyridine system is presented in Fig. 6.

Kinetic studies performed at different initial concentrations of $Re_2(CO)_6(OX)_2$ and its reaction partners have established that the dissociative solvolysis is first order with respect to each reactant. This indicates a complete chemical rearrangement allowing for the simple kinetic analysis if a high excess of the solvolysing agent (with concentration C_{solv}) is applied (pseudo-

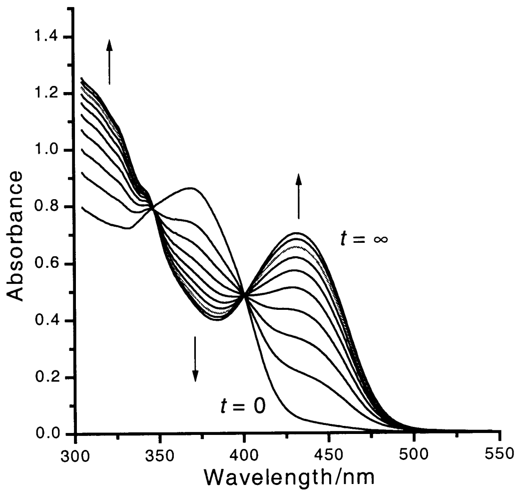

Fig. 6 Time evolution of UV-VIS absorption spectra (recorded at 100 s intervals) for 10^{-4} M solutions of $Re_2(CO)_6(OX)_2$ in dichloromethane after addition of pyridine (0.413 M).

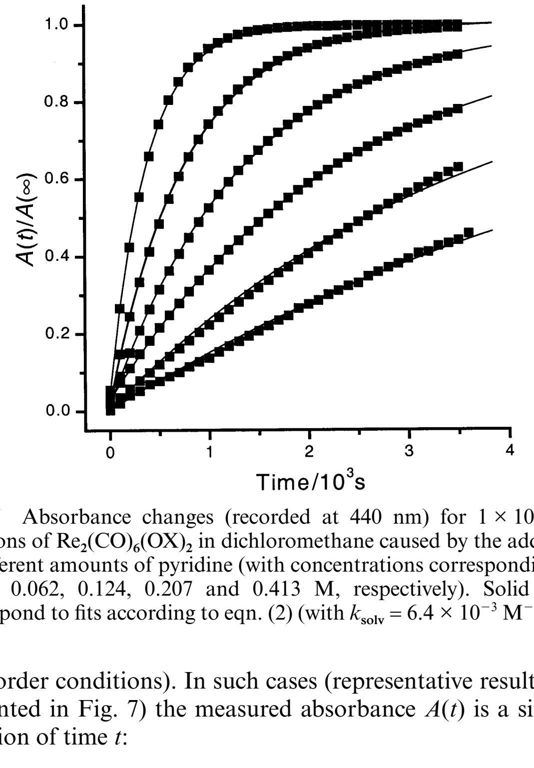

Fig. 7 Absorbance changes (recorded at 440 nm) for 1×10^{-4} M solutions of $Re_2(CO)_6(OX)_2$ in dichloromethane caused by the addition of different amounts of pyridine (with concentrations corresponding to 0.033, 0.062, 0.124, 0.207 and 0.413 M, respectively). Solid lines correspond to fits according to eqn. (2) (with $k_{solv} = 6.4 \times 10^{-3}$ M^{-1} s^{-1}).

zero order conditions). In such cases (representative results are presented in Fig. 7) the measured absorbance $A(t)$ is a simple function of time t:

$$\frac{A(t)}{A(\infty)} = 1 - \exp(-k_{solv}C_{solv}t) \qquad (3)$$

where k_{solv} is the solvolysis rate constant.

The rates of the studied processes have been found to roughly correlate with the solvolysing agent donicity: $k_{solv} = 0.6 \times 10^{-3}$, 2.9×10^{-3}, 6.2×10^{-3} and 6.4×10^{-3} M^{-1} s^{-1}, for ACN (DN = 14.1), DMF (26.6), DMSO (29.8) and pyr (33.1), respectively. On the other hand, the corresponding k_{solv} value found for hexamethylphosphorous triamide (HMPT, DN = 38.8) of 2.0×10^{-3} M^{-1} s^{-1}, is significantly lower than would be provided from this simple correlation, suggesting that other factors (*e.g.*, steric factor relating to the large HMPT molecules) influence the overall reaction. The results of kinetic studies allow us to propose a plausible mechanism for the solvolysis reaction. Most probably, due to the observed second order of the total reaction, addition of only one solv molecule to the dimeric $Re_2(CO)_6(OX)_2$ complex is enough to cause its dissociation into $Re(CO)_3(OX)$solv and $Re(CO)_3(OX)$ products. In the second stage reaction of $Re(CO)_3(OX)$ with a second electron donating molecule takes place, resulting in the formation of the next $Re(CO)_3(OX)$solv molecule. Although our studies do not let us conclude which stage is the slowest one, it can be speculated that it is the attack of the first donor molecule on the dimeric $Re_2(CO)_6(OX)_2$.

It should be emphasised that the equilibria established during the course of the kinetic experiments with relatively weakly coordinating agents such as ethyl acetate (EA) and acetone (AC) are significantly different. The final absorbance is much lower than in "pure" solutions indicating only partial dissociation, which seems to be understandable. Similar results have been obtained in very weakly coordinating media like nitromethane (DN = 2.7), toluene (DN ≈ 0.1) or chlorobenzene solutions. UV-VIS absorption and/or emission spectra of these solutions correspond to superposition of bands characteristic for the monomeric and dimeric species. It should be noted that several hours are necessary for equilibrium to be established in these systems. The fact that only the dimeric $Re_2(CO)_6(OX)_2$ precipitates from a toluene solution suggests that the discussed process is reversible. In a similar way, heating of the solid $Re(CO)_3$solv sample under high vacuum also leads to dimeric $Re_2(CO)_6(OX)_2$. However, dimerisation of the monomeric $Re(CO)_3(OX)$solv, where solv is a strong electron donor, seems to be unachievable in solution.

Concluding remarks

The applied synthetic methods yield new $Re(CO)_3^+$ complexes, the monomeric ones of the general formula $Re(CO)_3(OX)$solv and the dimeric one $Re_2(CO)_6(OX)_2$ with structures confirmed by means of X-ray measurements. IR as well as UV-VIS absorption/emission investigations indicate that the dimeric $Re_2(CO)_6(OX)_2$ undergoes dissociative solvolysis in a wide range of solvents, with the exception of extremely poorly donating solvents (*e.g.*, DCM). The products $Re(CO)_3(OX)$solv prove to be stable and once coordinated the solv molecule is not removable, at least in the cases of rather strong donors (*e.g.*, pyridine). Nevertheless, the solvolysis reaction of $Re_2(CO)_6(OX)_2$ in poorly coordinating media (*e.g.*, toluene) is reversible. In the course of the preparation of $Re_2(CO)_6(OX)_2$ any contact with solvents other than DCM or toluene should be avoided because it may lead to contamination of the reaction product as most probably occurred in the cited work[28] (crystallisation of the crude product from an ethyl ether–acetone mixture). Different purification procedures may explain small differences between UV-VIS absorption spectra recorded in our work and presented previously.[28]

Monomeric $Re(CO)_3(OX)$solv and dimeric $Re_2(CO)_6(OX)_2$ complexes exhibit different photophysical properties. A particularly interesting feature of $Re_2(CO)_6(OX)_2$ is the fact that this compound displays structured fluorescence, suggesting that the excited state is completely ligand localised. The LE nature of the emissive state agrees quite well with the large shift between absorption and emission bands caused by intraligand charge shift of electron density from the lone pairs of the phenolic oxygen to the nitrogen atom.[29–31] Room temperature emission bands of the monomeric $Re(CO)_3(OX)$solv complexes have hardly any structure, which indicates that the emitting states have mixed IL/MLCT character. Another interesting property of $Re_2(CO)_6(OX)_2$ is the fact that this compound displays no phosphorescence at all, while the complexes of the $Re(CO)_3(OX)$solv type do. It may be also explained by a change in the excited triplet character from "pure" IL to IL/MLCT (lack of the IL phosphorescence is observed for free 8-hydroxyquinoline).[45,46] The observed differences in spectroscopic behaviour are probably caused by a shift of the Re d orbitals to lower energy ($Re(CO)_3solv^+$ fragment seems to be a better electron donor in comparison to $Re(CO)_3^+$). It should be noted, however, that in the case of dimeric $Re_2(CO)_6(OX)_2$ both π-systems of the coordinated 8-quinolinato ligands are positioned almost antiparallel to each other, with a mean distance between them in the range of a few angstroms which may lead to excitonic interaction between both Re(CO)$_3$(OX) subunits. Currently available spectroscopic data do not allow us to discuss this option in more detail until results from the emission polarisation studies are available.

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