

A luminescent tricarbonylchlororhenium(I) complex featuring a flexible “crown ether” ligand. Manipulation of photoexcited state properties *via* binding of small cations †

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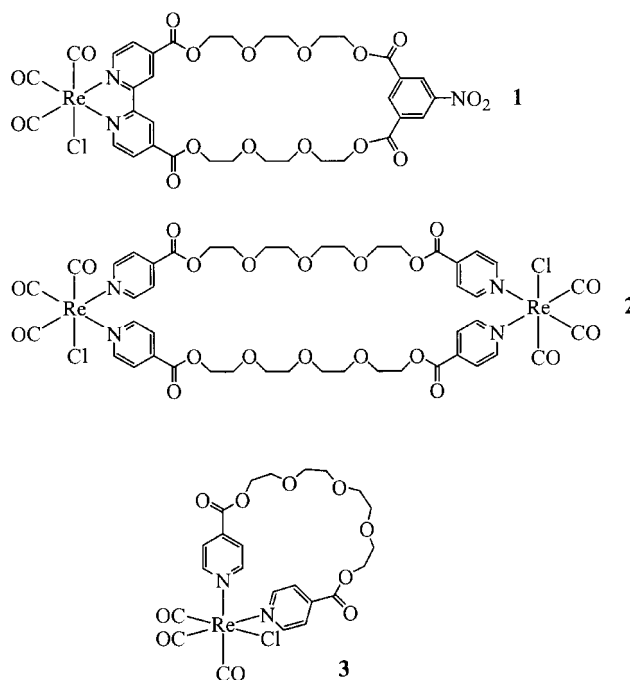
A luminescent complex, $[\text{Re}(\text{CO})_3(\text{Cl})(\text{LL})]$ where LL is 1,11-bis(4-pyridylcarboxy)-3,6,9-trioxaundecane, was prepared, and the crystal structures of two solvates were determined. The flexible polyether chain of the chelating ligand adopts an all *gauche* conformation about the aliphatic C–C bonds, and does not appear to introduce any appreciable constraints on the geometry at the octahedral metal center. The cavity formed by the “crown ether” has a diameter of *ca.* 7 Å. Binding of cations causes a decrease of the luminescence lifetime of the $\text{Re}^{\text{III}}\text{LL}^-$ excited state, consistent with an “energy gap” effect and with a rapid excited-state equilibrium between bound and unbound moieties. Binding constants were determined for several alkali metal ions, and for the ammonium cation. The chemical affinity of the crown-functionalized ligand is not specific for any of the cations studied, but, instead, is similar for a range of cations. Comparative studies with a complex containing ester-functionalized pyridine ligands, but lacking the polyether linkage necessary to form the crown, also showed excited state binding of small cations, indicating that the anionic ester pyridyl fragment, rather than the polyether fragment, is responsible for the binding.

Introduction

With the goal of understanding long-range electron transfer between donors and acceptors which are not covalently linked, we have been studying crown-ether linked assemblies, in which a chromophoric metal-ligand photo excited state donor is linked to an organic acceptor *via* macrocyclic ether spacers.^{1,2} The polyether spacer serves as a recognition or encapsulation site for non-covalently bound organic or inorganic molecules which can facilitate or inhibit long distance electron transfer between the donor and acceptor sites. We have recently reported³ the crystal structure of such an inorganic donor/organic acceptor compound **1**. In solution, as well as in the solid state, this complex adopts a folded conformation where the donor ($\text{Re}(\text{bipy})$) and acceptor (nitrobenzene) sites are coplanar and in close proximity to one another. A related complex can undergo a conformational change in solution, from an unfolded to a folded structure, as the temperature is lowered; notably, the folding has a marked effect on electron-transfer reactivity.²

Larger polyether cavities were sought, and although larger cyclic crown-pyridine or crown-bipyridine assemblies could be prepared in low yield,⁴ good synthetic routes did not prove readily accessible. We reasoned that asymmetric inorganic donor/inorganic acceptor complexes, in which the metal centers are bridged with two pyridine-functionalized polyether ligands, might prove more accessible. If this were the case, the length of the polyether chain could be varied with minimum synthetic effort. In order to test this hypothesis, the preparation of a symmetric dinuclear metal complex **2**, in which two $\text{Re}(\text{CO})_3(\text{Cl})$ moieties are bridged by two 1,11-bis(4-pyridylcarboxy)-3,6,9-trioxaundecane ligands, was attempted, but only the mononuclear compound **3**, was isolated.

fac- $\text{Re}^{\text{I}}(\text{CO})_3$ -Based imine and diimine complexes are typically luminescent, and in some cases the luminescence has been



exploited for molecular sensing purposes. For example, complexes with azacrown substituted 2,2'-bipyridine and 1,10-phenanthroline ligands,⁵ or a pyridine derivative,⁶ have been used as luminescent sensors for alkali- and heavy-metal cations. A cationic “molecular square” complex containing alternating Re and Pd corner atoms displays a modest propensity for recognition of complex anions, where the cavity based recognition event is signaled by an increase in the luminescence intensity.⁷ We find that compound **3** is similarly luminescent, but that the luminescence can be quenched by alkali or metal ammonium cations. Quantitative studies indicate that the quenching is associated with binding of the cations. Realistically, the

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/3407/>

Table 1 Selected bond lengths (Å) and angles (°) for the two solvates of compound **3**

	Triclinic	Monoclinic	
Re1–Cl1	2.489(2)	2.447(3) ^a	2.406(5) ^b
Re1–N1	2.233(6)	2.203(4)	
Re1–N2	2.262(6)	2.216(4)	
Re1–C21	1.901(9)	1.919(6)	
Re1–C22	1.912(8)	1.927(6)	
Re1–C23	1.964(9)	1.89(1) ^a	1.896(8) ^{b,c}
O8–C21	1.18(1)	1.145(6)	
O9–C22	1.18(1)	1.149(6)	
O10–C23	1.11(1)	1.13(1) ^a	1.221(8) ^{b,c}
C11–Re1–N1	85.4(2)	88.9(1) ^a	87.1(2) ^b
C22–Re1–C23	87.9(3)	89.4(6) ^a	86.46 ^b
C11–Re1–N2	89.5(2)	86.5(2) ^a	88.8(2) ^b
C11–Re1–C21	86.1(3)	93.6(2) ^a	90.9(2) ^b
C11–Re1–C22	96.1(2)	89.2(2) ^a	94.7(2) ^b
C11–Re1–C23	173.9(2)	176.9(7) ^a	178.5(6) ^b
N1–Re1–N2	83.8(2)	82.2(2)	
N1–Re1–C21	95.0(3)	94.3(2)	
N1–Re1–C22	174.7(3)	177.9(2)	
N1–Re1–C23	91.1(3)	92.4(6) ^a	91.8(6) ^b
N2–Re1–C21	175.5(3)	176.5(2)	
N2–Re1–C22	91.1(3)	96.9(2)	
N2–Re1–C23	95.1(2)	90.9(7) ^a	90.1(6) ^b
C21–Re1–C22	90.2(3)	86.6(2)	
C21–Re1–C23	89.3(4)	89.2(7) ^a	90.1(6) ^b

^a Disordered, occupancy = 0.60. ^b Disordered, occupancy = 0.40. ^c Constrained bond length.

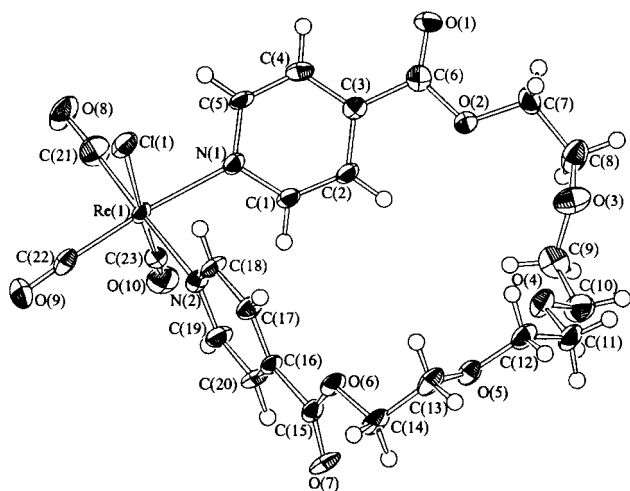


Fig. 1 An ORTEP drawing of the dichloromethane solvate of compound **3** showing the numbering scheme. Thermal parameters are represented at the 50% probability level.

binding constants are too small to be of interest for sensing applications. On the other hand, the changes in excited state lifetime and emission quantum yield that accompany weak cation binding are substantial. In addition to photophysical studies, we undertook a crystallographic study in order to determine the conformation of the crown ether fragment; the crystals structure of two solvates of **3** are reported.

Results and discussion

Crystal structures

An ORTEP⁸ drawing of the dichloromethane solvate (triclinic form) of compound **3** is shown in Fig. 1. Selected bond lengths and angles for both solvates are listed in Table 1. The complexes have the expected geometry around the octahedral metal center, with bond lengths in the expected range for *fac*-Re(CO)₃(Cl) fragments. The Re–N bonds range from 2.203(4) to 2.262(6) Å.

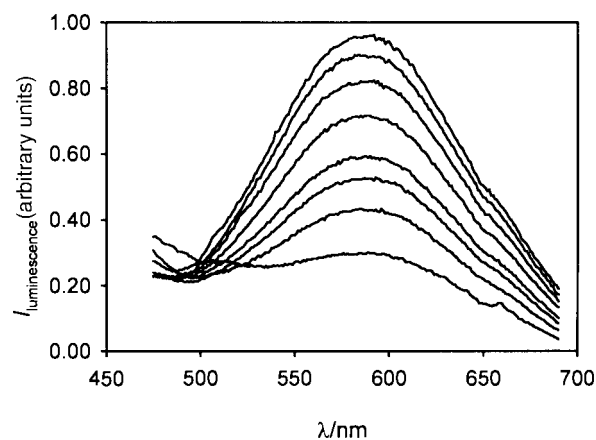


Fig. 2 Decrease in luminescence of compound **3** with addition of LiClO₄ in air-saturated acetone as solvent.

The usual range for Re–N distances in Re(CO)₃(Cl)(L)₂ complexes with monodentate nitrogen donor L ligands is 2.20–2.26 Å.^{8–11} The polyether chain does not appear to constrain the geometry of the pyridine groups at the rhenium center, the N–Re–N angles being less than 8° away from the ideal 90° value. This angle, in related Re(CO)₃(Cl)(L)₂ complexes with monodentate L ligands, has been observed in the 82–87° range.^{9–11} The flexible polyether chain adopts an all *gauche* conformation around the single C–C bonds, with most torsion angles close to –73 or +73°, while the C–O–C–C angles are all *trans*. Other flexible crown ether derivatives have also shown a propensity to adopt mostly *gauche* O–C–C–O conformations.¹² The main difference (at the metal centers) between the two solvates is the conformation of the pyridine rings: in the triclinic dichloromethane solvate one of the pyridine ligands is tilted –10.1(5)° away from the Cl–Re–C–O axis, while the other is tilted by 44.2(6)°, adopting a conformation similar to what has been reported for [Re(CO)₃(Cl)(py)₂] and [Re(CO)₃(Cl)(4,4'-bipy)₂] (*ca.* –130, –38 and –56°),¹¹ [Re(CO)₃(Cl)(quin)₂] (quin = quinoline) and [Re(CO)₃(Cl)(iquin)₂] (iquin = isoquinoline) (*ca.* 45 °C).⁹ In the water solvate (monoclinic form) the pyridine rings are tilted by *ca.* 40–45°.

Luminescence and binding studies

The most obvious difference between the Re^I–crown system studied here and related cation-responsive Re–crown assemblies is that, typically, the latter are based on an aza-crown binding site (molecular recognition site) connected to a reporter (variable luminescent metal center) *via* a bipyridine or phenanthroline ligand.^{5,6} The available tertiary amine group (N nitrogen lone pair) of the aza crown reductively quenches the luminescence of the nominally triplet, metal-to-ligand (imine) charge-transfer excited state. Cation binding increases the oxidation potential of the amine group, thereby inhibiting reductive quenching and restoring luminescence intensity.¹³

In contrast, compound **3** is initially luminescent, and addition of an alkali metal or ammonium cation causes a striking decrease in luminescence intensity (Fig. 2). The corresponding Stern–Volmer plots display negative curvature, an indication that the quenching mechanism is not purely dynamic, but instead involves chromophore/quencher binding. We initially assumed that the binding or host moiety must be the flexible difunctional polyether ligand, which, when co-ordinated, should behave as a crown ether. The assumption was supported by a control study involving [Re(CO)₃(Cl)(4-Phpy)₂] (4-Phpy = 4-phenylpyridine): emission from this compound, which lacks the putative binding site, is unaffected by Li⁺ addition. Further experiments (detailed below) showed, however, that the binding motif employed by **3** is more subtle than we initially thought.

Binding was quantified, for a range of cations in both

Table 2 Equilibrium constants for cation binding by compound **3**^a

Solvent	Quencher	K_b/M^{-1}
Acetone	NH_4PF_6	25 ± 2
	$LiClO_4$	19.6 ± 0.6
	$NaSCN$	17 ± 1
	$NaPF_6$	18 ± 9
	$KSCN$	27 ± 4
Acetonitrile	NH_4SCN	25 ± 5
	NH_4PF_6	31 ± 2
	$LiClO_4$	32 ± 6
	$LiClO_4^b$	47 ± 11
	$NaClO_4$	7.8 ± 0.6
Tetrahydrofuran	$KSCN^c$	6.2 ± 1.1
	$NaClO_4$	6.2 ± 3

^a Determined from luminescence intensity, at room temperature in air-saturated solvent, unless noted otherwise. ^b Determined from variable-concentration lifetime experiments, in deoxygenated solvent. ^c Binding constant should be interpreted with caution: control experiments with $[(CH_3(CH_2)_3N)SCN]$ indicated partial luminescence quenching at concentrations higher than *ca.* 0.02 M in acetonitrile, despite the probable steric prohibition of cation binding. One explanation would be the onset of an alternative slow bimolecular redox quenching reaction involving thiocyanate oxidation.

acetone and acetonitrile as solvents, by fitting the cation concentration-dependent luminescent response of compound **3** to expression (1) where I_0 and I_i are the initial and concentration-

$$I_i = I_0 + (\Delta I K_b C)/(1 + K_b C) \quad (1)$$

variable luminescence intensities, respectively, ΔI is the extrapolated maximum change in intensity, C the concentration of the cation and K_b the binding constant. The results of these experiments are reported in Table 2. The data show that only weak binding takes place between **3** and the cations studied. As opposed to cyclic crowns and azacrowns, the cyclic ligand cavity is not particularly specific to the identity of the cation, but, rather, binds a range of target analytes. In acetone the binding selectivity is particularly poor, with binding constants ranging from 17 ± 1 to $27 \pm 4 M^{-1}$. In acetonitrile, however, selectivity is somewhat greater, with binding constants ranging from *ca.* $6\text{--}8 M^{-1}$ for Na^+ and K^+ to *ca.* $25\text{--}32 M^{-1}$ for NH_4^+ and Li^+ .

Since the bound cations clearly must be innocent with respect to electron transfer and electronic energy transfer, the range of potential explanations for the quenching phenomenon is rather limited. In view of the probable metal-to-ligand (rhenium-to-pyridine) charge transfer nature of the emissive excited state, we suggest that the role of the bound cation is to stabilize, in an electrostatic sense, the co-ordinated pyridine radical anion, thereby lowering the excited-state/ground-state energy gap, ΔE . From the known inverse relationship between ΔE and the log of the rate constant for non-radiative decay for this class of compounds (*i.e.* "energy gap law" behavior),¹⁴ an increase in $k(\text{non-radiative})$ and corresponding decreases in emission intensity and excited-state lifetime, τ , would be expected to accompany cation complexation. (Related tricarbonylrhenium imine and diimine excited state decays are known to be dominated by non-radiative kinetics.¹⁴ For **3**, in the absence of electrolyte, we obtained an emission quantum yield of 0.002, implying dominant non-radiative decay here as well.)

Consistent with the energy gap idea, we find (Fig. 3) that τ decreases from 50 ± 6 to *ca.* 10 ns upon addition of Li^+ ; a fit of the lifetime data by an expression analogous to eqn. (1) yields a binding constant of $47 \pm 11 M^{-1}$, in good agreement with the steady-state spectrofluorimetric determination. Curiously, τ decreases only gradually with increasing Li^+ concentration, *i.e.* lifetimes of intermediate lengths are observed at moderate Li^+ concentrations. One might instead have anticipated overlapping decays corresponding to a mixture of filled host ($3 \cdot M^+$) and

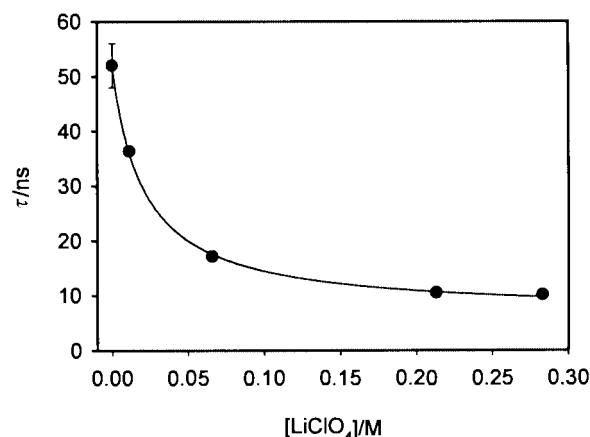
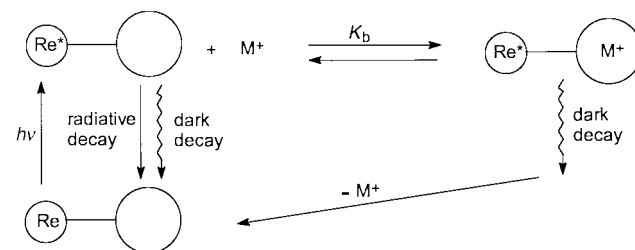


Fig. 3 Dependence of the luminescence lifetime of compound **3** on the concentration of added $LiClO_4$ in air-saturated acetonitrile as solvent. Fitting of the data yields $K_b = 47 \pm 11 M^{-1}$.

empty host (**3**) species having lifetimes of ≈ 10 and 50 ns, respectively; behavior of this kind is not seen. Also surprising is the apparent constancy of the emission energy, at least at low and moderate cation concentrations (Fig. 2). From the known energy gap behavior of closely related tricarbonylrhenium imine complexes, an energy gap decrease (and a red shift in emission energy) of *ca.* $1500 cm^{-1}$ should accompany the observed 4- to 5-fold decrease in excited-state lifetime.¹⁴

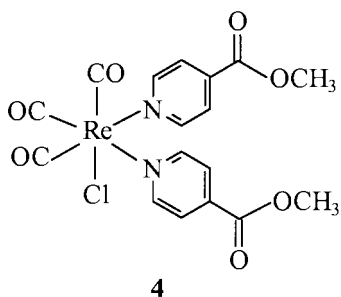
To account for the combined observations of variable lifetimes and approximately invariant emission energies, we propose the excited-state equilibrium shown in Scheme 1. Accord-



Scheme 1

ing to this scheme, the observed emission under all conditions (except, perhaps, the conditions of highest Li^+ concentration) comes from free compound **3**. In the presence of Li^+ , however, the effective lifetime of **3** is shortened due to dynamic equilibration with the shorter lived (*ca.* 10 ns) and non-emissive (or only poorly emissive) $3 \cdot Li^+$ excited-state assembly. For the scheme to be viable, of course, the $3/3 \cdot Li^+$ excited-state equilibration would need to occur rapidly. From the observed equilibrium binding constant ($32 M^{-1}$ in acetonitrile), and assuming a diffusion-limited binding rate constant, say $\approx 10^{10} M^{-1} s^{-1}$, an unbinding or dissociation rate constant of *ca.* $3 \times 10^8 s^{-1}$ is obtained (where $k_{\text{unbind}} = k_{\text{bind}}/K_b$). The corresponding lifetime for unbinding would be $\tau_{\text{unbind}} = 1/k_{\text{unbind}} \approx 3$ ns, a value compatible with the notion of dynamic equilibration in a 10 to 50 ns time frame. Finally, a corollary to Scheme 1 is that the binding constants recorded in Table 2 describe cation association with the excited-state form of **3**, rather than ground state **3**.

Given the apparent importance of localized coulombic interactions in binding the alkali metal ions, we also examined compound **4**¹ which contains a pair of ester functionalized pyridines but lacks the three additional ether oxygens of **3**. Like **3**, but in contrast to $[Re(CO)_3(Cl)(4\text{-Phpy})_2]$, **4** binds alkali metals when photo excited: $K(Li^+) = 70 \pm 20 M^{-1}$. We conclude that electrostatic interactions between the guest and the pyridine anion and ester oxygens, but not the ether oxygens, of the photo-excited host species, **3**, account for the propensity of the excited complex to bind the guest.



Conclusion

The reaction of 1,11-bis(4-pyridylcarboxy)-3,6,9-trioxaundecane with $[\text{Re}(\text{CO})_5(\text{Cl})]$ leads to a mononuclear complex, by co-ordination of the bidentate polyether ligand, which results in a cavity of *ca.* 7 Å diameter. The aliphatic chain appears to be sufficiently flexible to permit an unconstrained geometry at the metal center, although one of the pyridine rings in the triclinic form adopts a conformation which differs from those normally observed in $\text{Re}(\text{CO})_3(\text{Cl})(\text{L})_2$ complexes with monodentate ligands. In the MLCT excited state, but not in the ground state, the complex weakly binds a range of simple cations, where binding appears to be driven by localized coulombic interactions with the transiently created anionic pyridine ester fragment rather than with the available polyether fragment. Despite the comparative weakness of the association, the bound cations exert a strong influence upon the excited state lifetime and emission quantum yield. The effects are tentatively ascribed to electrostatic stabilization of the excited state (in an energetic sense), diminution of the excited-state/ground-state energy gap, and consequent acceleration of the rate of excited-state non-radiative decay.

Experimental

Synthesis of compound 3

The 1,11-bis(4-pyridylcarboxy)-3,6,9-trioxaundecane ligand was prepared by reflux of 0.9 mL (5 mmol) of tetraethylene glycol, 2.8 mL (16 mmol) of isonicotinoyl chloride hydrochloride and 2.5 mL of triethylamine in 200 mL of methylene chloride under a nitrogen atmosphere for 4 h. After cooling to room temperature, the reaction mixture was washed with a saturated aqueous NaHCO_3 solution, and dried over anhydrous Na_2SO_4 , after which time the organic solution was boiled with activated charcoal and filtered. The filtrate was evaporated to a colorless oil, which solidified upon drying *in vacuo*, to yield the bidentate ligand (2.1 g, quantitative) (Found: C, 58.9; H, 6.1; N, 6.8. $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_7$ requires C, 59.4; H, 6.0; N, 6.9%). The metal complex 3 was prepared by heating to reflux 433 mg (1.1 mmol) of ligand with 419 mg (1.2 mmol) of $[\text{Re}(\text{CO})_5(\text{Cl})]$ in toluene for 4 h. The solvent was removed by rotatory evaporation, redissolved in methylene chloride, and evaporated again. The residues were separated on a silica column, using ethyl acetate as eluent (310 mg, 41%) (Found: C, 39.0; H, 3.4; N, 3.9. $\text{C}_{23}\text{H}_{24}\text{ClN}_2\text{O}_{10}\text{Re}$ requires C, 38.9; H, 3.4; N, 4.0%).

Crystal structure determination

Crystals suitable for X-ray diffraction were obtained by recrystallization in methylene chloride–hexanes. Data were collected on a Nonius CAD-4 diffractometer, or with a Bruker Smart 1000 CCD with graphite monochromatized Mo-K α radiation ($\lambda = 0.7107$ Å). They were corrected for absorption (analytical correction).¹⁵ The structures of both solvates were solved by direct methods,¹⁶ and refined using the TEXSAN software package.¹⁷ Atomic scattering factors were taken from the usual sources.¹⁸ Hydrogen atoms were calculated at idealized positions. Refinement was carried out using full matrix least squares on F^2 .

Table 3 Crystal data for compound 3

	Dichloromethane solvate	Water solvate
Formula	$\text{C}_{24}\text{H}_{27}\text{Cl}_3\text{N}_2\text{O}_{10}\text{Re}$	$\text{C}_{23}\text{H}_{26}\text{ClN}_2\text{O}_{11}\text{Re}$
<i>M</i>	796.05	728.03
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
<i>a</i> /Å	10.312(3)	14.8661(11)
<i>b</i> /Å	12.391(2)	16.9066(12)
<i>c</i> /Å	13.020(3)	11.6709(8)
α /°	63.94(1)	—
β /°	84.54(2)	111.654(1)
γ /°	80.56(2)	—
<i>V</i> /Å ³	1474(1)	2726.3(3)
<i>T</i> /K	173	152
<i>Z</i>	2	4
μ (Mo-K α)/cm ⁻¹	45.05	46.08
Measured reflections	4817	25150
Unique reflections	4527	6757
Reflections used in refinement	4527	6757
<i>R</i> _{int}	0.015	0.056
<i>wR</i> (<i>F</i> ²) _{all}	0.127	0.083

Crystal data for both solvates can be found in Table 3. In the triclinic dichloromethane solvate one chloride of the methylene chloride solvent molecule is disordered over two positions. Occupancy factors of 0.5 were obtained for the disordered chlorides (Cl3a, Cl3b), which were constrained so that the sum of their occupancy factors equals unity. In the monoclinic water solvate the CO/Cl disorder was refined with the occupancy factors for the two models equaling unity. Refinement converged with a 0.60:0.40 population ratio. The water molecule associated with O11 is hydrogen bonded to polyether O atoms. Although H atoms could not be located, short O...O separations within hydrogen-bonding range are observed (O3...O11a 3.02(2); O7...O11c 2.93(2); O6...O11c ‡ 2.98(2); O7...O11a ‡ 3.23(2); O3...O11c 3.26(3) Å).

CCDC reference number 186/1607.

See <http://www.rsc.org/suppdata/dt/1999/3407/> for crystallographic files in .cif format.

Luminescence measurements

Luminescence measurements (binding constants and quantum yield) were made by using an ISA Fluorolog-3 spectrofluorimeter, with an excitation wavelength of 360–370 nm, and 5 nm excitation and emission slits. Binding constants were determined by monitoring the intensity of luminescence at $\lambda_{\text{em}} = 586$ nm. Luminescence lifetimes were measured by using the 337 nm N_2 laser line of a PRA LN1000 nitrogen laser (5 Hz, 300–700 ps pulse width) as the excitation source. Lifetimes were obtained by fitting the data by a single exponential decay. Quantum yield measurements and variable concentration lifetime measurements were done in solvent which was deoxygenated with N_2 . The binding constants reported in Table 2 were determined in air-saturated solvent. The quantum yield of compound 3 was estimated using $[\text{Re}(\text{CO})_3(\text{Cl})(4\text{-Phpy})_2]$ as a standard.¹⁹

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‡ $x, \frac{3}{2} - y, -\frac{1}{2} + z$.

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