CO₂ capture by Mn(I) and Re(I) complexes with a deprotonated triethanolamine ligand†

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CO₂ capture at low concentration by catalysts is potentially useful for developing photocatalytic and electrocatalytic CO₂ reduction systems. We investigated the CO₂-capturing abilities of two complexes, fac-Mn(X₂bpy)(CO)₃(OCH₂CH₂NR₂) and fac-Re(X₂bpy)(CO)₃(OCH₂CH₂NR₂) (X₂bpy = 4,4’-X₂-2,2’-bipyridine and R = -CH₂CH₂OH), which work as efficient catalysts for CO₂ reduction. Both complexes could efficiently capture CO₂ even from Ar gas containing only low concentration of CO₂ such as 1% to be converted into fac-Mn(X₂bpy)(CO)₃OC(O)(OCH₂CH₂NR₂) (M = Mn and Re). These CO₂-capturing reactions proceeded reversibly and their equilibrium constants were >1000. The substituents of X₂bpy strongly affected the CO₂-capturing abilities of both Mn and Re complexes. The density functional theory (DFT) calculation could be used to estimate the CO₂-capturing abilities of the metal complexes in the presence of triethanolamine.

Introduction

The catalytic conversion of CO₂ into useful carbon resources by using sustainable energy such as sun light has attracted much attention as one of the technologies that address the issues of both global warming and the shortage of carbon-based resources. Transition metal complexes with ions such as Re(I),¹ Mn(I),² Ru(II),³ Ir(III),⁴ Ni(II),⁵,6 Fe(II),⁵,6 and Co(II)⁷,8 have been reported as one of the sensitiser unit and fac-Re(BL)(CO)₃(OCH₂CH₂NR₂) (BL = bridging ligand) as a catalyst unit shows almost same the photocatalytic efficiency and selectivity for CO₂ reduction in an atmosphere of 10% CO₂ as that in a 100% CO₂ (0.13 M in solution) atmosphere. Even at 0.5% CO₂ concentration, its photocatalytic efficiency was still about 60% of that at 100% CO₂ concentration. These results suggest that the ability of metal complex catalysts to capture CO₂ using the deprotonated TEOA ligand potentially offers an effective method for reducing low-concentration CO₂ atmospheres without the need for condensation.

Although some similar CO₂ insertion reactions into the M–OR bond of other alkoxide metal complexes, such as M = Mn(II)⁹,10 and Re(I)⁹,10 and R = -CH₃ and -C₂H₅, have been reported,¹⁴–16 systematic and quantitative research, especially into the effects of different ligands and/or different central metal ions on the CO₂ capture reactions, has not yet been reported to the best of our knowledge.
Here we report the CO₂ capture abilities of Mn(II) 4,4′-X₂-bpy tricarbonyl complexes, where X is any substituent of the corresponding Re(I) complexes, i.e., X = H, Br, and MeO; fac-Mn(X₂bpy)(CO)₃(OCH₂CH₂NR₂) efficiently captured CO₂ in the same manner as the Re(I) complexes but the corresponding W(0) bpy tricarbonyl complex did not. The abilities of the Mn(II) complexes to capture CO₂ were different from those of the corresponding Re(I) complexes and the abilities of both the Mn(II) and Re(I) complexes were strongly dependent on the substituents on the diimine ligand. We successfully clarified the reasons for these dependences of the CO₂ capture abilities by using density functional theory (DFT) calculations.

Results and discussion

Ligand substitution of fac-[M(X₂bpy)(CO)₃(MeCN)]⁺ in a DMF–TEOA mixed solution

As a typical example, fac-[Mn(bpy)(CO)₃(MeCN)]⁺ (5.0 mM) was added to an Ar-saturated DMF solution containing TEOA (1.3 M), and the changes in the vibrational bands of the CO ligands (ν(CO)) were followed by FT-IR. In Fig. 1, the peaks at ν(CO) = 2046 and 1970 cm⁻¹ were attributed to the starting complex and their intensity gradually decreased and new absorption bands appeared over time. After 30 min, there were no more changes in the IR spectrum and the main bands were observed at ν(CO) = 2040, 1943, and 1936 cm⁻¹, which are attributed to fac-[Mn(bpy)(CO)₃(DMF)]⁺ (1Mn-bpy) based on the similarity of the highest wavenumber peaks to those of the starting complex in the case of the Re(I) complex.

Some shoulder peaks were also observed at ν(CO) = 2020 and 1900 cm⁻¹. Fig. 2a shows the IR spectra measured several hours after dissolving the same complex into DMF solutions containing different concentrations of TEOA. As the concentration of TEOA in the solution was changed from 1.3 to 3.9 or 4.5 M, the changes in the concentration of the solvent did not strongly depend on the TEOA concentration. This was probably due to a Mn(II) complex with an imidate ester ligand, i.e., fac-[Mn(bpy)(CO)₃{−NH=C(CH₃)-OCH₂CH₂NR₂}]⁻ (3Mn-bpy), which is produced by the addition of deprotonated TEOA to the MeCN ligand (Fig. 1, right scheme). The difference in the totally symmetric vibrational band from fac-[Mn(bpy)(CO)₃(MeCN)]⁺ was Δν(CO) = 16 cm⁻¹, and a similar peak shift was observed when fac-[Mn(bpy)(CO)₃(MeCN)]⁺ was dissolved in a MeCN-TEOA (5 : 1, v/v) solution (Δν(CO) = 14 cm⁻¹, Fig. S2†). This identification is also supported by the fact that the difference in ν(CO) between fac-[Re(bpy)(CO)₃(MeCN)]⁺ and fac-[Re(bpy)(CO)₃{−NH=C(CH₃)-OCH₂CH₂NR₂}]⁻ was Δν(CO) = 13 cm⁻¹. This reaction was much slower in the case of the Mn(II) complex than that of the corresponding Re(I) complex. To further clarify the identity of this minor product, the following experiment was performed. fac-[Mn(bpy)(CO)₃(MeCN)]⁺ was dissolved in a DMF solution containing 1.3 M TEOA. After 60 min, additional TEOA or DMF was added to this solution, i.e., the concentration of TEOA in the solution was changed from 1.3 to 3.9 or 0.65 M. The changes in the concentration of the solvent did not affect the concentration of the minor product in either case (Fig. S2†). This suggests that the minor product was 3Mn-bpy, which was only produced by the reaction between fac-[Mn(bpy)(CO)₃(MeCN)]⁺ and TEOA, was stable in the solution. In other words, the presence of 3Mn-bpy in the solution should not affect the equilibrium between 1Mn-bpy and 2Mn-bpy. Therefore, in the following discussion, we consider only the equilibrium between the DMF and TEOA complexes.

![Image](image_url)

Fig. 1 Changes in the IR spectra of fac-[Mn(bpy)(CO)₃(MeCN)]⁺ (5.0 mM) in a DMF solution containing TEOA (1.3 M) under an Ar atmosphere over 30 min: 1-Mn-bpy, 2-Mn-bpy, 3-Mn-bpy.
There are two possible equilibrium equations (eqn (1) and (3)) for the conversion of 1Mn-bpy into 2Mn-bpy. In the mechanism described in eqn (3), one TEOA molecule works as both a nucleophile and a base. In the case of eqn (1), two TEOA molecules contribute to the ligand substitution reaction, where proton capture from the TEOA interacting with the metal centre by the other TEOA molecule is considered. In this ligand substitution, the main mechanism is probably described in eqn (1) because the solution contained a very high concentration of TEOA (>1.3 M). Therefore, we chose eqn (1) for the DFT calculation as described below. In eqn (2), the concentration of the protonated TEOA ([H−TEOA]+) was assumed to be the same as that of 2Mn-bpy because the proton that originated in the TEOA ligand should be captured by another TEOA molecule as described above. The concentrations of the Mn(n) complexes were calculated by curve-fitting of the IR spectra and were used to determine the equilibrium constant, i.e., $K_1$(Mn-bpy) = (0.22 ± 0.03) $\times 10^{-3}$, by using eqn (2).

\[
K_1(\text{Mn-bpy}) = \frac{[2\text{M-bpy}][\text{DMF}] + \text{H-TEOA}^+}{[\text{1M-X-bpy}][\text{TEOA}^2]} = \frac{[2\text{M-bpy}][\text{DMF}]}{[\text{1M-X-bpy}][\text{TEOA}^2]}.
\]

When the Mn complexes with substituents at the 4,4′-position of the bpy ligand, i.e., fac-[Mn(X2bpy)][CO]3(MeCN)] (X = Br and OMe), were dissolved in the DMF–TEOA mixed solution, similar IR spectral changes were observed in both cases (Fig. S4†). However, the equilibrium constants were very different from $K_1$(Mn-bpy). Electron-withdrawing substituents gave a larger constant, i.e., $K_1$(Mn-Br2bpy) = (0.64 ± 0.03) $\times 10^{-3}$. On the other hand, electron-donating substituents gave a smaller constant, i.e., $K_1$(Mn-(MeO)2bpy) = (0.12 ± 0.01) $\times 10^{-3}$. These results strongly suggest that stronger electron-withdrawing substituents on the X2bpy ligand give rise to higher stability of 2Mn-X2bpy.

In the case of the corresponding Re(i) complex, fac-[Re(X2bpy)][CO]3(MeCN)] was converted into fac-[Re(X2bpy)][CO3]- (DMF) (1Re-X2bpy) by first dissolving in DMF § and then into fac-[Re(X2bpy)][CO3]-OCH2CH2NR2 (2Re-X2bpy) by the addition of TEOA to the solution because this procedure could suppress the formation of [Re(bpy)][CO3]-(NH=C(CH3)-OCH2CH2NR2)] (3Re-bpy). The equilibrium constants between 1Re-X2bpy and 2Re-X2bpy are summarised in Table 2. The values of $K_1$(Re-X2bpy) are consistent with those of the corresponding Mn complexes as described above, i.e., the electron-withdrawing substituents on the X2bpy ligand yielded a larger equilibrium constant. The equilibrium constant of the Re complexes was much larger than that of the corresponding Mn complexes, for example, $K_1$(Re-bpy) = ($71 \pm 1$) $\times 10^{-3}$ and $K_1$(Mn-bpy) = (0.64 ± 0.03) $\times 10^{-3}$, that is, the formation of 2Mn-X2bpy was thermodynamically less favourable compared to that of the corresponding Re(i) complex in the DMF–TEOA mixed solution.

CO2 capture by fac-M(X2bpy)(CO)3(OCH2CH2NR2)

Introduction of CO2 into the DMF–TEOA solution containing the equilibrium mixture of 1Mn-bpy and 2Mn-bpy caused rapid disappearance of the vCO bands attributed to 1Mn-bpy and 2Mn-bpy and the appearance of three new vCO bands at 2028, 1936, and 1913 cm$^{-1}$ (Fig. 3a). When this CO2-saturated solution was bubbled with Ar for 30 min, the original vCO bands of 1Mn-bpy and 2Mn-bpy were fully recovered (Fig. S5†). These IR spectral changes are very similar to those of the corresponding Re(i) complexes, where both 1Re-bpy and 2Re-bpy were converted into the CO2 adduct complex fac-[Re(bpy) CO3][OC(O)OCH2CH2NR2] (4Re-bpy) upon bubbling with CO2. These results strongly suggest that CO2 capture by the Mn(i) complex proceeded well and that the reaction was reversible. Identification of the CO2 adduct was confirmed by 1H and 13C NMR experiments in a DMSO-d6 solution containing TEOA.

DMF-d7 was not used because the signal of a carbonate carbon (M–OC(O)O–R) is expected to be observed at a similar magnetic field to that of the amide carbon of DMF. We confirmed that even in a DMSO–TEOA mixed solution, similar IR spectral changes occurred to those in the DMF–TEOA solution (Fig. 3b). The 1H NMR spectra of the solution containing the Mn complexes were first measured under an Ar atmosphere and then measured again after bubbling with CO2 for 3 min (Fig. S6†). The 1H NMR signals attributed to the bpy ligands changed completely before and after bubbling with CO2; the proton peaks attributed to the bpy ligands cause rapid changes were observed under an Ar atmosphere, disappeared and four new proton signals were observed at a higher magnetic field under a CO2 atmosphere. Fig. 4a shows the 13C NMR spectrum with proton decoupling; a singlet peak attributable to the carbonate carbon (M–OC(O)O–R) at 158.7 ppm was observed under the CO2 atmosphere. This signal was drastically enhanced by using 13CO2 (99% 13C content).

Fig. 3 IR spectra of the equilibrated mixture of 1Mn-bpy and 2Mn-bpy in DMF (a) or DMSO (b) containing TEOA (1.3 M) after Ar bubbling (red line) and CO2 bubbling (blue line) for 15 min.
instead of CO2 (Fig. 4b). Without proton decoupling, the signal at 158.7 ppm became a triplet with $J_{	ext{C-H}} = 3.8$ Hz (Fig. 4c). This is attributable to long-range coupling with the methylene group in the deprotonated TEOA moiety of the carbonate ester ligand (Fig. 4) because a similar signal was reported in the $^{13}$C NMR spectrum of $3\text{Re-bpy}$ (158.4 ppm, 3.6 Hz). These results strongly suggest that the insertion reaction of CO2 into the Mn–O bond in $2\text{Mn-bpy}$ gives the complex $\text{fac-[Mn(bpy)(CO)3(OC(O)OCH2CH2-\text{NR2})]}(\text{4Mn-bpy})$ (eqn (5)).

As shown in Fig. 5a, the ratios of the peaks changed with the CO2 concentration in the solution. We successfully conducted curve-fitting to obtain the concentrations of $1\text{Mn-bpy}$, $2\text{Mn-bpy}$ and $4\text{Mn-bpy}$ as shown in Fig. 5b. Direct determination of $K_d(\text{Mn-bpy})$ from the peak area of $2\text{Mn-bpy}$ showed a large experimental error because the peak of $2\text{Mn-bpy}$ was very small. Therefore, $K_d(\text{Mn-bpy})$ was calculated by using eqn (7) with $K_f(\text{Mn-bpy})$ and $K_d(\text{Mn-bpy})$, which is the equilibrium constant between $1\text{Mn-bpy}$ and $4\text{Mn-bpy}$ (eqn (6) and (7)). In eqn (7), the concentration of the protonated TEOA ($\text{[H-TEOA^+]}$) was assumed to be the same as the total concentrations of $2\text{Mn-bpy}$ and $4\text{Mn-bpy}$ because of the same reason in the case of eqn (2). This calculation method gave much lower experimental error; the value of $K_d(\text{Mn-bpy})$ between $2\text{Mn-bpy}$ and $4\text{Mn-bpy}$ was obtained to be $(61 \pm 12) \times 10^3$ M$^{-1}$.

**Comparison of the CO2-capturing abilities of the Mn(i), Re(i) and W(0) complexes**

As described in the previous section, both series of the Mn(i) and Re(i) complexes have high CO2-capturing abilities (Scheme 3). The CO2 insertion reactions into $2\text{Mn-X2bpy}$ were more favourable than those into $2\text{Re-X2bpy}$, equilibrium constants of which are defined as $K_d(\text{M-X2bpy})$ (M = Mn and Re) (Process 2). However, the CO2-capturing ability of $1\text{Mn-X2bpy}$ in the presence of TEOA was small.

**Table 1** Equilibrium constants of the Mn complexes

| Metal | $K_d/10^{-3}$ | $K_d/10^3$ M$^{-1}$ | $K_d/M^{-1}$ |
|-------|--------------|---------------------|--------------|
| H     | 0.22 ± 0.03  | 61 ± 12             | 14 ± 1       |
| Br    | 0.64 ± 0.03  | 42 ± 8              | 27 ± 4       |
| MeO   | 0.12 ± 0.01  | 84 ± 15             | 10 ± 1       |
was lower than that of 1Re-X_{bpy}, and the equilibrium constants are defined as $K_1[M-X_{bpy}]$ (Process 3). This is because the formation of the TEOA adducts ($2Mn-X_{bpy}$ and $2Re-X_{bpy}$), i.e., Process 1, is much more favourable in the case of the Re complexes, the equilibrium constants of which are $K_{1}[M-X_{bpy}]$.

1Re-Br_{bpy} as the starting complex most efficiently captured CO$_2$ from gases containing low concentrations of CO$_2$ in DMF including 1.3 M TEOA where the volume ratio between DMF and TEOA is 5 : 1; bubbling air containing only 400 ppm of CO$_2$ (1.7 $\times$ 10$^{-4}$ M in solution) into the DMF–TEOA mixed solution containing 1Re-Br_{bpy} and 2Re-Br_{bpy} converted 31% of the Re complexes into the corresponding CO$_2$ adduct, i.e., 4Re-Br_{bpy}. This conversion ratio increased by changing the solvent to DMSO. In a DMSO solution containing 1.3 M TEOA, 4Re-Br_{bpy} formed at a 47% ratio under air.

Since the W(0) complex with a structure similar to that of the Re(I) and Mn(I) complexes has been reported, we checked the ligand substitution and CO$_2$-capturing ability of fac-W(bpy)(CO)$_3$(MeCN). This complex was synthesised by dissolving W(bpy)(CO)$_4$ into an MeCN solution, which was refluxed under an Ar atmosphere overnight. Evaporation of the solvent gave fac-W(bpy)(CO)$_3$(MeCN) as a brown solid containing a small amount of W(bpy)(CO)$_4$. Since fac-W(bpy)(CO)$_3$(MeCN) was air-sensitive and W(bpy)(CO)$_4$ did not affect the following experiments, we used this solid.[1]

The FT-IR spectrum of fac-W(bpy)(CO)$_3$(MeCN) in an MeCN solution showed carbonyl vibration bands at $\nu_{CO} = 1898$ and 1782 cm$^{-1}$ (Fig. S8†), which are consistent with a previous report.[4] This complex was dissolved in a DMF solution, and a CO vibration band at $\nu_{CO} = 1887$ cm$^{-1}$ attributable to fac-W(bpy)(CO)$_3$(DMF) was observed (Fig. S9†). The other $\nu_{CO}$ bands overlapped with the carbonyl vibrational band of the DMF solvent and small absorption bands at $\nu_{CO} = 2005$, 1875, and 1831 cm$^{-1}$ were attributed to fac-W(bpy)(CO)$_4$, which had the same wavelength and strength as those observed in the MeCN solution (Fig. 6). Addition of TEOA into the DMF solution containing W(bpy)(CO)$_3$(DMF) did not affect the $\nu_{CO}$ band at all under an Ar atmosphere. In addition, the CO vibration of fac-W(bpy)(CO)$_3$(DMF) in the IR spectra did not change after bubbling CO$_2$ through this solution (Fig. 6). These results clearly indicate that fac-W(bpy)(CO)$_3$(OCH$_2$CH$_2$NR$_2$) did not form from fac-W(bpy)(CO)$_3$(DMF) even in the presence of 1.3 M TEOA, and the CO$_2$-capturing reaction also did not proceed under these reaction conditions (refer the equation in Fig. 6).

**Gibbs free energy change and DFT calculation**

The Gibbs free energy ($G$) changes in Processes 1–3 were calculated by using the equilibrium constants ($K_1$, $K_2$, and $K_3$) and are summarised in Table 3 (values in parentheses).
The observed abilities of the metal tricarbonyl complexes in the CO2-capturing reactions involving TEOA were examined based on the DFT calculations. Selected geometrical parameters calculated at the def2-SVP/PBE1PBE level including solvent effects are depicted in Table S2.† All of the Mn–N(bpy) and Mn–C(CO) bond lengths were calculated for 1Mn-bpy, 2Mn-bpy and 4Mn-bpy with the singlet spin state and were in good agreement with those of the X-ray structure determined for fac-Mn(CO)3(bpy)4⁺,⁴⁹ supporting the accuracy of the DFT calculation. The geometrical optimisation of 1Re-bpy, 2Re-bpy and 4Re-bpy also gave molecular structures with geometrical parameters similar to those of the X-ray structure of fac-Re(CO)3(bpy)OC6H5n.⁷⁸

The CO stretching vibrational frequencies of the tricarbonyl complexes were calculated for the DFT-optimised structures and were corrected using the reported scaling factor (Tables S3 and S5†).⁷⁸ While all of the calculated νCO values were slightly higher than the observed ones, the differences in νCO are almost constant for each series of the tricarbonyl complex: 31–50 cm⁻¹ for Mn(i) complexes and 16–23 cm⁻¹ for Re(i) complexes. The constant deviation in the calculated νCO supports the experimental identification of the species involved in the CO2-capturing reactions.

The changes in Gibbs free energy (ΔG°) of each process for the Mn(i) and Re(i) complexes were then calculated based on the DFT calculations (Table 3). For the overall reaction (Process 3), these calculated ΔG° values are in good agreement with those obtained by the experiments with an error of 5 kJ mol⁻¹ (∼1 kcal mol⁻¹).

For CO2 capture by the Mn complexes, the calculated ΔG° for reaction 1 is about 9–14 kJ mol⁻¹ lower than the observed value, while those for Process 2 are 13–17 kJ mol⁻¹ higher. This trend is also seen in the Re complexes even though the differences are smaller compared to those of the Mn complexes. These results are probably caused by an overestimation of the free energy formation for the M–TEOA complexes (2M-X_bpy). The TEOA moiety with three ethanol groups has several conformational isomers. The geometrical optimisation of 2Mn-X_bpy and 4Mn-X_bpy gave somewhat compact structures due to intramolecular hydrogen bonding between the metal-coordinating O atom and the two remaining OH groups in the TEOA moiety.

The lengths of the hydrogen bonds in 4Mn-X_bpy are around 1.76–1.81 Å. On the other hand, in the case of 2Mn-X_bpy, the hydrogen bonds between the anionic O atom, which is attached to the metal ion, and the OH groups are considerably shorter (1.50–1.59 Å) (Fig. S10†). The same effects were observed in the Re complexes as well. Such strong intramolecular hydrogen bonding in 2M-X_bpy is one of the reasons for the overestimation of their stabilisation energies because, in the DMF–TEOA mixed solution, intermolecular hydrogen bonds with other TEOA molecules could break such a compact conformation and several other stable conformations would be formed. A more accurate prediction of ΔG° for the CO2 insertion reaction therefore requires the evaluation of the TEOA conformational distribution including explicit interactions with other TEOA molecules. It should be noted that this uncertainty should not affect the ΔG° values of Process 3 because 2Mn-X_bpy and 2Re-X_bpy do not contribute to this process as shown in the equation for determining K3 (Scheme 3). In other words, the errors based on the overestimation of the stabilisation energy of 2Mn-X_bpy and 2Re-X_bpy can be cancelled between Processes 1 and 2.

As described in the previous section, there are two possible equilibrium equations (eqn (1) and (3)) for the ligand substitution of DMF by TEOA. However, in solutions containing high concentration of TEOA (1.3 M), the reaction with one TEOA molecule acting as both a nucleophile and a base is considered unfavourable. The DFT calculation also supports this consideration because the observed νCO values (1902, 1918 and 2017 cm⁻¹) are close to those calculated for 2M-bpy rather than for 2M-bpy-H⁺ (see Tables S3 and S4†). In addition, the calculated ΔG° corresponding to eqn (3) (14.5 kJ mol⁻¹) is higher than the ΔG° value for Process 1 (10.1 kJ mol⁻¹), which also indicates the favourability of eqn (1).

For the CO2-capturing reaction of the corresponding W(CO)3(bpy)X species, the ΔG° values for Processes 1, 2, and 3 are calculated to be +21.8, −9.0, and +12.8 kJ mol⁻¹, respectively. The calculated large positive ΔG° value of Process 3 is consistent with the results showing that the W(0) complex was less reactive for the CO2-capturing reaction in the presence of TEOA compared to the Re(i) and Mn(i) complexes.

As shown for the three series of metal complexes consisting of different metal ions and different ligands, DFT was able to calculate the ΔG° values for the overall CO2-capturing reaction (Process 3) with good accuracy (∼5 kJ mol⁻¹). We can use this method for estimating the CO2-capturing abilities of other metal complexes and to examine the mechanism of CO2-capturing reactions.

**Experimental section**

**General procedures**

FT-IR spectra were measured using a JASCO FT/IR-610 or 6600 spectrometer at 1 cm⁻¹ resolution. ¹H NMR and ¹³C NMR spectra were measured in acetonitrile-d₃, DMF-d₇ or DMSO-d₆.

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### Table 3 Calculated and experimental changes in the Gibbs free energy (ΔG°) of reactions 1–3 for the Mn(i), Re(i) and W(0) complexes

| Metal | Reaction | Process 1 | Process 2 | Process 3 |
|-------|----------|-----------|-----------|-----------|
| Mn(i) | Process 1 | 10.1      | -15.3     | -5.2      |
|       |          | (20.9)    | (-27.3)   | (-6.4)    |
| Br    | Process 1 | 8.9       | -15.0     | 6.1       |
|       |          | (18.2)    | (-26.4)   | (-8.2)    |
| OMe   | Process 1 | 10.5      | -10.3     | +0.2      |
|       |          | (22.4)    | (-28.1)   | (-5.7)    |
| Re(i) | Process 1 | -8.0      | -2.6      | 10.6      |
|       |          | (6.35)    | (-17.6)   | (-11.1)   |
| Br    | Process 1 | 7.1       | -25.6     | -17.8     |
|       |          | (5.09)    | (-18.0)   | (-12.9)   |
| OMe   | Process 1 | 11.2      | -16.7     | -5.5      |
|       |          | (8.67)    | (-19.5)   | (-10.8)   |
| W(0)  | Process 1 | 21.8      | -9.0      | 12.8      |

° Values in parentheses denote the experimental values calculated using ΔG° = -RTlnK using T = 298 K and K₁, K₂ and K₃.
using a JEOl ECA400-II at 400 and 100 MHz, respectively. Electrospray ionisation mass spectroscopy (ESI-MS) was performed using a Shimadzu LCMS-2010A system with acetonitrile as the mobile phase.

Materials

DMF was distilled under reduced pressure after pre-drying using activated molecular sieves of 4 Å and stored under Ar in a glove box. TEOA was distilled under reduced pressure and stored under Ar in a glove box. DMSO was distilled under reduced pressure after pre-drying overnight with CaH2 and distilled again by CaH2 before use. All other reagents of reagent-grade quality were used without further purification.

Calculation of equilibrium constants

Preparation procedures of the solutions for the measurements were performed in a glove box (UNICO, UN-650F) with a gas circulation dehydration device (DGE-05) under Ar (water content was less than 376 ppm). Concentrations of the complexes in solutions were obtained by the peak areas of \( \nu_{\text{CO}} \) at the highest wavenumber (2000–2060 cm\(^{-1} \)) in the IR spectra. The peak areas attributed to each complex were obtained by curve-fitting using a linear combination of the Gaussian and the Lorentzian functions.

Ligand substitution reaction

The Mn(i) and W(0) diimine tricarbonyl acetonitrile complexes were dissolved in DMF solutions containing different concentrations of TEOA. The solutions were kept at room temperature in the dark for several hours and then their IR spectra were measured. In the case of the Re(i) complexes, the complexes with an acetonitrile ligand were dissolved in DMF to avoid the formation of \( \text{ReX}_2\text{bpy} \). The solutions were kept at room temperature in the dark for several hours (3 h), when all of the complexes were converted into \( \text{ReX}_2\text{bpy} \), and then TEOA was added to these solutions. After keeping the solutions at room temperature in the dark for 2 h, the IR spectra of the equilibrium mixtures were recorded.

CO2-capturing reactions

Various amounts (0.020–0.025 mL) of a CO2-saturated DMF solution (the concentration of CO2 is 0.20 M) \(^{18,19}\) were added to DMF solutions (1.8 mL) containing TEOA (1.3 M) and the equilibrium mixture of the metal complexes in a shielded sample tube by using a micro-syringe in a glove box. After the solutions were kept at room temperature for several hours, the IR spectra were measured.

Synthesis

\( \text{fac-Re(X}_2\text{bpy})(\text{CO})_3\text{Br} \) was synthesised according to a reported method.\(^ {1,2} \) \( \text{fac-Mn(X}_2\text{bpy})(\text{CO})_3\text{Br} \) was synthesised according to a reported method with a small difference indicated as follows.\(^ {15} \) All procedures for the synthesis of the Mn(i) complexes were performed in a dark room with red light. W(bpy)(CO)\(_4\) and \( \text{fac-W(bpy)(CO)}_3(\text{MeCN}) \) were synthesised according to a reported method.\(^ {23,24} \)

\( \text{fac-Mn(bpy)(CO)}_3(\text{MeCN})(\text{PF}_6) \), \( \text{fac-Mn(bpy)(CO)}_3\text{Br} \) (1.0 g, 2.7 mmol) and AgPF\(_6\) (0.69 g, 2.7 mmol) were dissolved in 350 mL of Ar-saturated acetonitrile and this solution was heated at 40 °C for 1 h. After cooling to room temperature, the white precipitate of AgBr was removed by filtration with a Celite phase, and the solvent was evaporated. A yellow residue was dissolved in a small amount of CH\(_2\text{Cl}_2\). \( \text{n-Hexane} \) was added to this solution to yield the target compound as a yellow precipitate, which was filtered and washed with a small amount of ether. Yield: 1.2 g (96%).\(^ {1} \) 1H NMR (400 MHz, chloroform-\( d_2 \)), ppm: \( \delta = 8.83 \) (d, 2H, \( \text{J} = 6.8 \text{ Hz} \), bpy-6,6\( \text{H} \)), 8.42 (d, 2H, \( \text{J} = 2.4 \text{ Hz} \), bpy-3,3\( \text{H} \)) 7.82 (d, 2H, \( \text{J} = 2.4, 6.8 \text{ Hz} \), bpy-5,5\( \text{H} \)), 2.16 (s, 3H, \( \text{NC-CH}_3 \)). FT-IR (MeCN): \( \nu(\text{CO})/\text{cm}^{-1} \) 2028, 1938, 1923. Elemental anal. calcd (%) for C\(_{13}\text{H}_{12}\text{BrMnN}_3\text{O}_3\text{PF}_6\): C, 28.20; H, 1.42; N, 6.58. Found: C, 28.50; H, 1.28; N, 6.69.

\( \text{fac-Mn(4,4'-dibromo-2,2-bipyridine)(CO)}_3(\text{MeCN})(\text{PF}_6) \). Yield: 0.45 g (95%).\(^ {1} \) 1H NMR (400 MHz, chloroform-\( d_2 \)), ppm: \( \delta = 8.76 \) (d, 2H, \( \text{J} = 6.8 \text{ Hz} \), bpy-6,6\( \text{H} \)), 8.42 (d, 2H, \( \text{J} = 2.4 \text{ Hz} \), bpy-3,3\( \text{H} \)) 7.82 (d, 2H, \( \text{J} = 2.4, 6.8 \text{ Hz} \), bpy-5,5\( \text{H} \)), 2.16 (s, 3H, \( \text{NC-CH}_3 \)). FT-IR (MeCN): \( \nu(\text{CO})/\text{cm}^{-1} \) 2051, 1963. Elemental anal. calcd (%) for C\(_{13}\text{H}_{11}\text{BrMnN}_3\text{O}_3\text{PF}_6\): C, 28.20; H, 1.42; N, 6.58. Found: C, 28.50; H, 1.28; N, 6.69.

\( \text{fac-Mn(4,4'-methoxy-2,2-bipyridine)(CO)}_3(\text{MeCN})(\text{PF}_6) \). Yield: 0.26 g (75%).\(^ {1} \) 1H NMR (400 MHz, chloroform-\( d_2 \)), ppm: \( \delta = 8.81 \) (d, 2H, \( \text{J} = 6.0 \text{ Hz} \), bpy-6,6\( \text{H} \)), 8.72 (d, 2H, \( \text{J} = 2.0 \text{ Hz} \), bpy-3,3\( \text{H} \)) 7.92 (d, 2H, \( \text{J} = 2.0, 6.0 \text{ Hz} \), bpy-5,5\( \text{H} \)), 2.06 (s, 3H, \( \text{NC-CH}_3 \)). FT-IR (MeCN): \( \nu(\text{CO})/\text{cm}^{-1} \) 2042, 1941. Elemental anal. calcd (%) for C\(_{13}\text{H}_{13}\text{BrMnN}_3\text{O}_3\text{PF}_6\): C, 23.39; H, 1.18; N, 5.46. Found: C, 23.56; H, 1.10; N, 5.62.

DFT calculations of changes in Gibbs free energy (\( \Delta G^0 \))

The geometry optimisations of chemical species involved in CO2-capturing were carried out using a hybrid density functional with 25% exchange and a 75% Perdew, Burke, and Ernzerhof correlation functional (PBE1PBE)\(^ {33} \) using a smaller def2-SVP basis set with an effective core potential for Re and Br
atoms. The solvent DMF was modelled as a dielectric continuum using a polarisable continuum model.\textsuperscript{44} The electronic energies were then obtained as the SCF energy of a single-point calculation on the optimised geometries using a larger basis set of def2-TZVP. The solvent effect of DMF was considered using the SMD method, a parametrised SCRF-based solvation model developed to predict the free energy of solvation.\textsuperscript{25,26} The thermal correction terms to evaluate the standard Gibbs energy of formation ($G_f$) were computed by vibrational frequency analysis of the stationary structures using the same calculation level as for the geometry optimisations. An appropriate scaling factor of 0.9817 was used for the computed zero-point energy.\textsuperscript{28} Changes in the Gibbs free energy ($\Delta G_f$) were calculated as the difference in $G_f$ between the reactants and the products. For the $\Delta G_f$ values corresponding to $K_2$ and $K_3$ with the unit of M$^{-1}$, the calculated $G_f$ values were corrected by $-7.9$ kJ mol$^{-1}$ for the change in the reference states from 1 bar to 1 M.\textsuperscript{29} All DFT calculations were executed using Gaussian 16 packages.\textsuperscript{37}

**Conclusions**

We found that the CO$_2$-capturing reactions of Mn(ii) diimine tricarbonyl complexes with a deprotonated TEOA ligand were similar to those of the corresponding Re(i) complexes. The equilibrium constants of both the Mn(i) and Re(i) diimine complexes for the ligand substitution (Process 1) and for CO$_2$ capture (Process 2) in DMF–TEOA solutions were determined. From the DFT calculations, in addition to these equilibrium constants, we systematically and quantitatively clarified the effects of both the metal and the substituents on the bpy ligand. This kind of metal affected both Processes 1 and 2. On the other hand, ligand substituents had a greater influence on Process 1 than Process 2. The DFT calculation can be applied to estimate the $\Delta G_f$ of the total reaction containing both the ligand substitution and CO$_2$ capture (Process 3), and the $\Delta G_f$ values were in good agreement with those calculated from the experimental data. The CO$_2$-capturing reaction of W(bpy)(CO)$_3$(DMF) in the TEOA–DMF solution did not proceed at all because of the large $\Delta G_f$ value for Process 3. These calculation approaches can give a good approximation to judge whether the total CO$_2$-capturing phenomenon (Process 3) proceeds or not with various metal complexes.

**Conflicts of interest**

There are no conflicts of interest to declare.

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