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Infrared spectroscopic and computational studies of $\text{Co}(\text{ClO}_4)_2$ dissolved in N,N -dimethylformamide (DMF). Vibrations of DMF influenced by Co^{2+} or ClO_4^- or both

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ABSTRACT

Infrared (IR) spectroscopy for N,N -dimethylformamide (DMF) shows that the OCN bend (δ_{OCN}) and the CO stretch (ν_{CO}) vibrations undergo an upshift and a downshift, respectively, on the dissolution of $\text{Co}(\text{ClO}_4)_2$. Quantum chemical calculations are performed for optimizing the structures and predicting the IR spectra of model complexes for solute species. The calculations reveal that Co^{2+} exerts a much larger influence than ClO_4^- on the vibrations of DMF. For $\text{Co}^{2+}(\text{DMF})_6$, in which each DMF molecule is coordinated to Co^{2+} via the O atom, the $\text{Co}^{2+}\cdots\text{DMF}$ interaction upshifts the δ_{OCN} frequencies ($+24\text{ cm}^{-1}$ on average) while the dipole coupling gives rise to splitting (12 cm^{-1}) of the modes. On the other hand, the $\text{Co}^{2+}\cdots\text{DMF}$ interaction downshifts the ν_{CO} frequencies (-15 cm^{-1} on average) while the splitting of the modes amounts to 37 cm^{-1} . As a result, one of the ν_{CO} modes is located at an upshifted position ($+13\text{ cm}^{-1}$) despite the O-atom coordination. For six-coordinated isomers of $\text{Co}^{2+}(\text{DMF})_7$, the δ_{OCN} and ν_{CO} frequencies of the second-sphere DMF are close to those of bulk DMF in neat liquid. The calculations indicate that it is difficult to prove or exclude the formation of contact ion pairs $[\text{Co}(\text{DMF})_5\text{ClO}_4]^+$ and solvent-shared ion pairs $[\text{Co}(\text{DMF})_6\text{ClO}_4]^+$ by IR spectroscopy in the δ_{OCN} and ν_{CO} regions. However, asymmetric ClO stretches of the ClO_4^- moiety suggest that conceivable is the coexistence of solvent-shared ion pairs only.

Keywords:

N,N-dimethylformamide; Cobalt (II) ion; Infrared spectroscopy; Quantum chemical calculations; Intermolecular interactions; Ion association

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1. Introduction

Formamide (FA), *N*-methylformamide (NMF), and *N,N*-dimethylformamide (DMF) have the general structure $\text{HC(=O)-NR}_1\text{R}_2$, where $\text{R}_1, \text{R}_2 = \text{H}$ for FA, $\text{R}_1 = \text{H}, \text{R}_2 = \text{CH}_3$ for NMF, and $\text{R}_1, \text{R}_2 = \text{CH}_3$ for DMF. These amides are high boiling-point liquids, miscible with most solvents, and capable of dissolving the majority of organic and inorganic compounds [1]. In previous studies for liquid structures of these amides [2–8], intermolecular interactions have been a major focus of interest. FA and NMF are protic solvents and can act as both proton donors and acceptors via their NH and CO groups, respectively, and are consequently able to form intermolecular $\text{NH}\cdots\text{OC}$ hydrogen bonds [2,3]. The definitive structure of liquid FA has not been established yet; models proposed so far include ring dimers, hydrogen-bonded chains, ring dimers with chains, ring hexamers, and so forth [4]. X-ray diffraction study indicated that NMF molecules form dimers and linear trimers leading to a chain-like structure connected by hydrogen bonds [3]. In contrast, DMF is aprotic; two methyl groups preclude the formation of $\text{NH}\cdots\text{OC}$ hydrogen bonds. Vibrational spectroscopic study concluded that DMF molecules form clusters oriented in a partially ordered way [5]. However, the cluster formation was not conclusive from NMR (nuclear magnetic resonance) measurements [6]. X-ray diffraction experiments with *ab initio* calculations indicated a disordered structure of liquid DMF, but a partially ordered structure was suggested with the formation of a cluster, possibly a dimer [7]. Recently, a highly developed local orientational structure was found in DMF, with the dipole moments preferentially oriented in an anti-parallel fashion [8].

A variety of experimental techniques have been applied for investigating coordination structures of metal ions in solution phase [9]. For instance, X-ray diffraction and EXAFS (extended X-ray absorption fine structure) methods have provided static structural information. Both methods were applied to $\text{Co}(\text{ClO}_4)_2$ dissolved in DMF [10,11]. The analysis of the data indicated that the Co^{2+} ion in DMF has an octahedral structure with six DMF molecules in the first solvation sphere. Meanwhile, vibrational spectroscopy has also been employed to probe the coordination of amide molecules to metal ions. Infrared (IR) and Raman spectroscopic

experiments were performed in the CO stretch region. For the three amides, characteristic frequency shifts of this mode were used to conclude the coordination via the O atom of the amides to Li^+ and Na^+ [12,13]. It was shown for DMF that the OCN bend frequency was also sensitive to the coordination to Li^+ [14], alkaline-earth metal ions [15], and first-row transition metal ions [15,16]. Theoretical calculations were carried out for model complexes of the $\text{Mg}^{2+}/\text{DMF}$ and $\text{Zn}^{2+}/\text{DMF}$ systems, but the purpose was to evaluate binding energies and structural parameters as functions of solvation numbers [15].

Ion association in amide solutions has also attracted attention, besides the interaction between the metal ion and amide molecules. Raman spectroscopy suggested the formation of both solvent-shared and contact ion pairs of Li^+ and ClO_4^- in DMF [14]. Dielectric relaxation study on LiClO_4 and NaClO_4 in DMF demonstrated that the alkali salts form predominantly solvent-shared ion pairs [17]. As for transition metal ions, IR spectra of $\text{Co}(\text{CF}_3\text{SO}_3)_2$ in DMF were interpreted by assuming the formation of contact ion pairs [18]. Meanwhile, Raman spectra of $\text{Cu}(\text{ClO}_4)_2$ in DMF showed no indication of solvent-shared or contact ion pairs [19]. It is highly desirable to complement the results of these spectroscopic studies with appropriate theoretical calculations.

In the present work, we have carried out IR spectroscopic studies of DMF solutions of $\text{Co}(\text{ClO}_4)_2$. The main purpose is not to provide new experimental data of high quality, but to make an accurate interpretation of the IR spectra. For this purpose, we have performed quantum chemical calculations for $\text{Co}^{2+}(\text{DMF})_6$ and $\text{ClO}_4^-(\text{DMF})_4$ complexes as models of Co^{2+} and ClO_4^- in DMF, respectively. Theoretical IR spectra of the model complexes have been compared with the experimental spectra in the regions of the OCN bend and CO stretch of DMF. $\text{Co}^{2+}(\text{DMF})_7$ complexes have also been studied in order to evaluate the effect of Co^{2+} on the vibrations of a DMF molecule in the second sphere. In addition, $[\text{Co}(\text{DMF})_5\text{ClO}_4]^+$, $[\text{Co}(\text{DMF})_6\text{ClO}_4]^+$, and $\text{Co}(\text{DMF})_5(\text{ClO}_4)_2$ complexes have been used to model contact, solvent-shared, and triple ion pairs, respectively. Effects have been examined of the ion pair formation on the OCN bend and CO stretch vibrations of DMF and also on asymmetric ClO stretches of ClO_4^- .

2. Experimental and computational methods

IR spectra are recorded on a Fourier transform IR spectrometer (JASCO, FT/IR-4100) equipped with an attenuated total reflection (ATR) unit (ATR PRO670H-S) and a ZnSe prism. ATR-IR spectra are obtained in the 650–4000 cm^{-1} region with a resolution of 2 cm^{-1} . The measurements are performed at ambient temperature. Cobalt perchlorate (Sigma-Aldrich) and DMF (Wako, purity $\geq 99.9\%$) are used as received. Solutions are prepared by addition of the salt to DMF liquid with concentrations up to 1.0 M.

Quantum chemical calculations are carried out with Gaussian 16 program package [20]. Density functional theory (DFT) method is employed by using the Becke's three parameter hybrid functional coupled with the Lee–Yang–Parr correlation functional (B3LYP). Dispersion interaction is corrected by addition of the D3 version of Grimme's dispersion with Becke–Johnson damping (GD3BJ) [21]. The second-order Møller–Plesset perturbation (MP2) method is also employed for energetics of selected species. Basis sets used are 6-311+G(2df) for Co and Cl while 6-31+G(d) for other atoms. With these basis sets we have been successful in reproducing the IR spectra for a series of solvated transition-metal ions ([22] and references therein). For species containing Co and other transition metals, SCF (self-consistent field) calculations sometimes end up with a solution that has an internal instability [22]. The stability of the SCF calculations is always checked until the lowest-energy solution is obtained. The ground state of Co^{2+} is ^4F with a $(3\text{d})^7$ configuration and the lowest doublet excited state (^2G) is by 203 kJ/mol higher in energy [23]. Therefore, only the quartet state is taken into consideration for complexes containing Co^{2+} . Self-consistent reaction field method with polarizable continuum model (PCM) is incorporated to implicitly account for extra solvent molecules surrounding the species of interest. Geometries of $\text{Co}^{2+}(\text{DMF})_n$ ($n = 1, 6\text{--}8$), $\text{ClO}_4^-(\text{DMF})_n$ ($n = 1$ and 4), $[\text{Co}(\text{DMF})_n\text{ClO}_4]^+$ ($n = 1, 5$, and 6), and $\text{Co}(\text{DMF})_5(\text{ClO}_4)_2$ complexes in PCM (solvent = DMF) are optimized without any symmetry constraints. The resulting structures are confirmed to have no imaginary-frequency vibration. Energies are reported after zero-point-energy correction

(ZPEC), unless otherwise stated.

Experimental values are available in the literature [24] for vibrational frequencies of DMF molecule in the gas phase. Harmonic frequencies of DMF in vacuum are calculated at the B3LYP-GD3BJ/6-31+G(d) level and the scaling factor is evaluated for each fundamental vibration. The results are 0.999 for the OCN bend (δ_{OCN}), 0.967 for the NCH bend (δ_{NCH}), and 0.970 for the CO stretch (ν_{CO}). The average value is 0.976 for six fundamental vibrations in the 1000–1800 cm^{-1} region. For all complexes in PCM, harmonic frequencies of DMF vibrations are scaled as follows. The δ_{OCN} and other vibrations below 1000 cm^{-1} are not scaled. Vibrations above 1000 cm^{-1} are scaled with the average factor of 0.976, while the δ_{NCH} and other vibrations in the 1350–1550 cm^{-1} region are scaled with 0.967 exceptionally. Meanwhile, the ClO stretches of the ClO_4^- unit in the complexes are scaled with a factor of 1.059, which is chosen to reproduce the 932 cm^{-1} band of ClO_4^- dissolved in DMF [14,19].

3. Results and discussion

3.1. IR spectra and structures of liquid DMF

Fig. 1a shows an ATR-IR spectrum of neat FA liquid in the 650–1800 cm^{-1} region. Prominent bands are assigned as follows [25,26]: the 658 cm^{-1} band to δ_{OCN} , the 1092 cm^{-1} to the CH_3 rock (ρ_{CH_3}), the 1387 cm^{-1} to δ_{NCH} , and the 1669 cm^{-1} to ν_{CO} . Note that these assignments are merely nominal, because many of the vibrational modes of DMF are of non-local character [25,26]. Fig. 1d displays expanded views of the δ_{OCN} (left) and ν_{CO} (right) regions of the experimental spectrum. The δ_{OCN} band can be represented by a single component centered at 658 cm^{-1} with a full width at half maximum (FWHM) of 4 cm^{-1} . The ν_{CO} band has an apparent FWHM of ≈ 30 cm^{-1} and can be decomposed into three components represented by Gauss functions centered at 1633, 1668, and 1682 cm^{-1} with FWHM values of 14, 15, and 23 cm^{-1} , respectively, although the intensity of the 1633 cm^{-1} component is extremely small.

Shundalau et al. published an IR spectrum of DMF diluted in CCl_4 (0.05 M) [27]. The ν_{CO} band was observed at 1686 cm^{-1} with a FWHM of ≈ 13 cm^{-1} . We carry out

B3LYP-GD3BJ calculations for a single DMF molecule in PCM (solvent = CCl₄); the resulting IR spectrum (Fig 1c, f) exhibits the ν_{CO} band at 1697 cm⁻¹. The position is close to the experimental maximum (1686 cm⁻¹) with the difference of less than the FWHM value. An IR spectrum for neat DMF was also published; the ν_{CO} band was observed around 1667 cm⁻¹ with a FWHM of ≈ 70 cm⁻¹ [27]. The band was decomposed into four components centered at 1630, 1655, 1671, and 1689 cm⁻¹. As expanded in Fig. 1d, our spectrum practically consists of two components centered at 1668 and 1682 cm⁻¹, which correspond to the latter two components of the previous spectrum. After Shundalau et al. [27], the 1668 cm⁻¹ component arises from DMF molecules strongly interacting with the neighbors while the 1682 cm⁻¹ component from the ones weakly interacting with the neighbors. Actually, the 1682 cm⁻¹ component coincides with the ν_{CO} band of DMF diluted in CCl₄ (1686 cm⁻¹).

The structure of liquid DMF has been studied both experimentally and theoretically. Fini and Mirone applied vibrational spectroscopy to liquid DMF [5]; they concluded that DMF molecules form clusters oriented in a partially ordered way. However, the cluster formation was not conclusive from NMR measurements [6]. Ohtaki et al. explored liquid DMF by X-ray diffraction and reported that intermolecular arrangement of DMF molecules in neat liquid is practically fully disordered and no evidence was found for the cluster formation [7]. From neutron diffraction studies, Basma et al. concluded that DMF molecules develop rich local ordering with the dipole moments preferentially oriented in an anti-parallel fashion [8]. The structures and IR spectra of monomer and clusters of DMF have been investigated by ab initio and DFT calculations [27–30]. The results relevant to the present work are summarized in section A.1 of Supplementary material (SM).

In analyzing the effect of Co²⁺ on the vibrations of DMF, it is convenient to define a theoretical IR spectrum of neat DMF liquid for a comparison with theoretical IR spectra of model complexes. We consider several model structures in order to mimic the intermolecular interactions in liquid DMF. The structures and theoretical IR spectra for the model dimers are described in section A.1 of SM. Fig. 1b, e displays the IR spectrum predicted from B3LYP-GD3BJ calculations for the most stable DMF dimer (D-v) in PCM.

The vibrational frequencies of D-v are as follows: 657.9/658.4 cm^{-1} for δ_{OCN} , 1088.7/1091.0 cm^{-1} for ρ_{CH_3} , 1385.3/1387.5 cm^{-1} for δ_{NCH} , and 1665.6/1669.0 cm^{-1} for ν_{CO} ; only the latter one of each mode has large IR intensity. Note that the B3LYP-GD3BJ calculations underestimate the intensity of the δ_{OCN} mode by one order of magnitude. Since the theoretical spectrum of D-v is in best agreement with the experimental spectrum, it is regarded as a mimic of the liquid DMF spectrum in the analysis presented below.

3.2. Interactions of DMF with Co^{2+} or ClO_4^- or both

Theoretical calculations are performed to predict the direction and magnitude of the shifts of the δ_{OCN} and ν_{CO} modes when a single DMF molecule interacts with Co^{2+} or ClO_4^- or both. For the $\text{Co}^{2+}(\text{DMF})_1$ complex, we consider monodentate coordination via the O or N atom of DMF and bidentate coordination via both O and N atoms. Owing to a smaller charge density on ClO_4^- than on Co^{2+} , the $\text{DMF}\cdots\text{ClO}_4^-$ interaction is expected to be much smaller than the $\text{Co}^{2+}\cdots\text{DMF}$ interaction. Nevertheless, we examine the effect of ClO_4^- on the vibrations of DMF in the $\text{ClO}_4^-(\text{DMF})_1$ complex. In addition, the possibility of ion association was pointed out for $\text{Co}(\text{CF}_3\text{SO}_3)_2$ dissolved in DMF [18]. Then we explore the $[\text{Co}(\text{DMF})_1\text{ClO}_4]^+$ complex in the forms of contact ion pairs and solvent-shared ion pairs. The results are described in section A.2 of SM. The point is that Co^{2+} exerts a much larger influence than ClO_4^- on the vibrations of DMF.

3.3. IR spectra of DMF solutions of $\text{Co}(\text{ClO}_4)_2$

Fig. 2 demonstrates changes in the δ_{OCN} (left) and ν_{CO} (right) regions of the IR spectra of DMF accompanied by gradual addition of $\text{Co}(\text{ClO}_4)_2$. These spectral changes are in agreement with those observed previously for similar systems [14–16, 18]. The ρ_{CH_3} band located around 1092 cm^{-1} is also known to be affected by metal ions [14,19]. However, the ρ_{CH_3} band is excluded from the analysis, because the vibrations of ClO_4^- obscure the spectral signature of the ρ_{CH_3} mode [14].

The ν_{CO} band of neat DMF practically consists of two components centered at 1668

(15) and 1682 (23) cm^{-1} , as described in section 3.1. The number in parenthesis stands for the FWHM value of each component. In order to decompose the spectrum of the 1.0 M solution, we need to add two more components centered at 1635 (28) and 1649 (12) cm^{-1} . We can reproduce the spectra of the 0.3 and 0.6 M solutions with these four components by adjusting only the relative intensities. With increasing the salt concentration, the relative intensity of the 1635 and 1649 cm^{-1} components increases gradually at the expense of the 1668 and 1682 cm^{-1} components. Similar spectral variation was reported for the LiClO_4 [31] and $\text{Co}(\text{CF}_3\text{SO}_3)_2$ [18] systems.

The δ_{OCN} band of neat DMF consists of a single component centered at 658 (4) cm^{-1} . In order to fit the spectra of the solutions, we need to add two more components centered at 663 ± 1 (5–6) and 684 ± 1 (6–9) cm^{-1} . With increasing the salt concentration, the 658 cm^{-1} component gets replaced by the 663 and 684 cm^{-1} components. Similar spectral variation was reported for Li^+ [14, 31], alkaline earth metal ions [15], first-row transition metal ions [15,16], and Cu^{2+} [19].

3.4. Structures and IR spectra of $\text{ClO}_4^-(\text{DMF})_4$

DMF is known to be a poor anion solvator [31]. Actually, MP2 calculations indicate that the interaction energy between ClO_4^- and DMF (12 kJ mol^{-1} for A-1-I) is much smaller than that between Co^{2+} and DMF (91 kJ mol^{-1} for 1-O-t). As a result, ClO_4^- exerts a much smaller influence than Co^{2+} on the vibrations of DMF, as demonstrated in section A.2 of SM. Accordingly, the interaction with Co^{2+} is expected to be responsible for the changes in the IR spectra of DMF upon dissolution of $\text{Co}(\text{ClO}_4)_2$. We confirm the expectation by carrying out calculations for the $\text{ClO}_4^-(\text{DMF})_4$ complex. Erkabaev et al. studied the solvation of ClO_4^- with acetonitrile (AN) molecules [32]. In the optimized structure of the $\text{ClO}_4^-(\text{AN})_4$ complex, four AN molecules solvate ClO_4^- separately in a tetrahedral arrangement. Then we look for a geometry of $\text{ClO}_4^-(\text{DMF})_4$ in which four DMF molecules are bound to ClO_4^- separately. Two examples are represented in Fig. 3a, b, which are the structures optimized from B3LYP-GD3BJ calculations. A-4-I (Fig. 3a) results from an

initial geometry in which each DMF is bound to ClO_4^- with a configuration similar to A-1-I (Fig. S3e), while A-4-II (Fig. 3b) from A-1-II (Fig. S3f). The energy difference between the two isomers is less than 2 kJ mol^{-1} (without ZPEC) from MP2 calculations at the DFT-optimized geometries. Fig. 3c–e compares the theoretical IR spectra of A-4-I and A-4-II with that of the model dimer D-v. For both A-4-I and A-4-II, the δ_{OCN} modes are located within $\pm 3 \text{ cm}^{-1}$ of the IR active mode of D-v. The ν_{CO} modes of A-4-I and A-4-II are downshifted by only -5 and -6 cm^{-1} on average, respectively. The magnitude of the shifts of the DMF vibrations caused by ClO_4^- is much smaller than that caused by Co^{2+} ; the latter is described later in section 3.5.

Although the separately solvating structures like A-4-i and A-4-ii seem to be appropriate for models of ClO_4^- in DMF solutions, they are not the lowest-energy structures of the $\text{ClO}_4^-(\text{DMF})_4$ complex. If we slightly modify the initial geometry of the optimization, it evolves to a structure in which DMF molecules form a cluster and ClO_4^- is associated with the exterior surface of the cluster. Such a structure lies typically 20 kJ mol^{-1} (without ZPEC) below A-4-I and A-4-II from MP2 calculations at the DFT-optimized geometries. The energetics indicates that the $\text{DMF}\cdots\text{DMF}$ interaction gets preference over the $\text{ClO}_4^-\cdots\text{DMF}$ interaction. This is one of the reasons why DMF is a poor solvator of ClO_4^- and other anions.

3.5. Structures and IR spectra of $\text{Co}^{2+}(\text{DMF})_6$

The analysis of the EXAFS spectra for DMF solutions of $\text{Co}(\text{ClO}_4)_2$ showed that the Co^{2+} ion adopts an octahedral coordination of six DMF molecules with the $\text{Co}\cdots\text{O}$ distance of $2.06 \pm 0.01 \text{ \AA}$ [10]. Accordingly, we employ the $\text{Co}^{2+}(\text{DMF})_6$ complex as a model of Co^{2+} in DMF solutions. Previously, we considered several isomers of the $\text{Li}^+(\text{FA})_6$ and $\text{Na}^+(\text{FA})_6$ complexes, which are classified into two groups [33]. All FA molecules are bound to the metal ion with ‘trans’ configuration in one group of isomers, while with ‘cis’ configuration in the other. In contrast, we fail to find stable $\text{Co}^{2+}(\text{DMF})_6$ complex in which all DMF molecules are bound to Co^{2+} with ‘cis’ configuration. If we choose such a structure as an

initial geometry, the subsequent optimization sometimes ends up with a structure in which a part of DMF molecules undergo reorientation and bind to Co^{2+} with ‘trans’ configuration, and sometimes ends up with a structure in which only five DMF molecules are bound to Co^{2+} .

Fig. 4 displays the structures of two isomers of $\text{Co}^{2+}(\text{DMF})_6$ with all DMF molecules are bound to Co^{2+} with ‘trans’ configuration. In both isomers, six O atoms of DMF adopt an octahedral coordination. Local dipole moment vectors of the CO bonds of three DMF molecules above Co^{2+} (illustrated by balls and sticks) make a left-hand turn in both 6-I (Fig. 3a) and 6-II (Fig. 3b). On the other hand, the vectors of three DMF molecules below Co^{2+} (illustrated by tubes) make a left-hand turn in 6-I whereas a right-hand turn in 6-II. 6-I is lowest in energy and 6-II is higher by 3 kJ mol^{-1} (without ZPEC) from MP2 calculations at the DFT-optimized geometries. Yokoyama et al. investigated the structures of solvated Co^{2+} in DMF by means of X-ray diffraction [10]. They reported that the distance from the Co^{2+} ion to each of O, carbonyl C, and N atom is 2.13 ± 0.02 , 2.99 ± 0.02 , and $4.23 \pm 0.02 \text{ \AA}$, respectively, corresponding to the $\text{Co}\cdots\text{O}-\text{C}$ bond angle of $122\text{--}123^\circ$. In 6-I, the distance from Co^{2+} to each atom is 2.11, 2.99, and $4.27 \text{ \AA}$, respectively, with the bond angle of 123° . In 6-II, the distance from Co^{2+} to each atom is 2.11, 3.00, and $4.28 \text{ \AA}$, respectively, with the bond angle of 124° . The geometrical parameters of 6-I and 6-II are in good agreement with the experimental data.

Fig. 5b, c represents the theoretical IR spectra predicted for 6-I and 6-II, respectively. Reproduced in Fig. 5a are the experimental IR spectrum of neat DMF liquid and the theoretical spectrum of the model dimer D-v. The experimental spectrum of the 1.0 M solution is reproduced in Fig. 5b. Table S3 of SM collects the frequencies and IR intensities of the δ_{OCN} and ν_{CO} modes of 6-I and 6-II along with the magnitude of the shifts relative to the IR active mode of D-v. IR active δ_{OCN} modes are predicted in the $682\text{--}683 \text{ cm}^{-1}$ region for 6-I and $682\text{--}684 \text{ cm}^{-1}$ for 6-II. The location is consistent with the 684 cm^{-1} component in the experimental spectra. Meanwhile, IR active ν_{CO} modes are predicted in the $1650\text{--}1653 \text{ cm}^{-1}$ region for 6-I and $1644\text{--}1654 \text{ cm}^{-1}$ for 6-II. The location is consistent with the 1649 cm^{-1} component in the experimental spectra. Overall, each of or a superposition of the

theoretical IR spectra for 6-I and 6-II is successful in reproducing the spectral components newly appeared on the dissolution of $\text{Co}(\text{ClO}_4)_2$.

Each of the six ν_{CO} modes of $\text{Co}^{2+}(\text{DMF})_6$ is not localized on a CO group of a particular DMF molecule but is delocalized over six DMF molecules. The highest-frequency ν_{CO} mode of 6-I at 1682 cm^{-1} involves in-phase motions of the CO groups of all DMF molecules. The IR intensity of this mode is almost zero because of the symmetry of the structure. The lowest-frequency mode of 6-I is located at 1645 cm^{-1} . The interval between the highest- and lowest-frequency ν_{CO} modes amounts to 37 cm^{-1} for both 6-I and 6-II. It has been considered that two major mechanisms cause a frequency shift of the ν_{CO} band of amide molecules in solutions: hydrogen bonding and transition dipole coupling [34]. As models of metal ions in FA solutions, we adopted the following complexes: $\text{Li}^+(\text{FA})_{5,6}$ [33], $\text{Na}^+(\text{FA})_6$ [33], $\text{Ca}^{2+}(\text{FA})_{7,8}$ [35], and $\text{Co}^{2+}(\text{FA})_6$ [36]. In the most stable isomer of each complex, FA molecules form $\text{NH}\cdots\text{OC}$ hydrogen bonds with their neighbors. Accordingly, both mechanisms, besides the influence of the metal ion, must be operative in shifting the frequencies of the ν_{CO} modes. In the $\text{Co}^{2+}(\text{DMF})_6$ complex, on the other hand, $\text{NH}\cdots\text{OC}$ hydrogen bonds are absent. For 6-I and 6-II, therefore, the splitting of 37 cm^{-1} should be caused primarily by the transition dipole coupling. In the meantime, the ν_{CO} modes are downshifted by -15 cm^{-1} on average as a result of the $\text{Co}^{2+}\cdots\text{DMF}$ interaction. Despite the binding of Co^{2+} to the O atom of DMF, the highest-frequency ν_{CO} mode of 6-I and 6-II shows an upshift of $+13\text{ cm}^{-1}$ relative to D-v, because the splitting caused by the transition dipole coupling is larger than the downshift caused by the metal ion. Note that there is an overlap of the frequency ranges between DMF molecules bound to Co^{2+} and free from Co^{2+} . In particular, the highest-frequency ν_{CO} mode of 6-I and 6-II coincides with the spectral component of neat DMF liquid that is assigned to DMF molecules weakly interacting with the neighbors (see section 3.1). One should keep this point in mind in making an assignment of the experimental spectra and in estimating the coordination number from a quantitative analysis of the band intensities.

The $\text{Co}^{2+}\cdots\text{DMF}$ interactions upshift the δ_{OCN} frequencies ($+24\text{ cm}^{-1}$ on average)

while the dipole coupling gives rise to splitting of the modes with an interval of 12 cm^{-1} . In contrast to the ν_{CO} modes, the magnitude of the shift is larger than that of the splitting of the modes. As a result, the frequency ranges are well separated between DMF molecules bound to Co^{2+} and free from Co^{2+} .

3.6. Structures and IR spectra of $\text{Co}^{2+}(\text{DMF})_7$

Next, we turn our attention to the $\text{Co}^{2+}(\text{DMF})_7$ complex. It is successful to find a potential-energy minimum corresponding to a seven-coordinated structure (7-VI, Fig. S5f of SM) with all DMF molecules bound to Co^{2+} . Nevertheless, one of the $\text{Co}\cdots\text{O}$ bonds ($2.47\text{ \AA}$) is longer than the average of the other six bonds ($2.18\text{ \AA}$). MP2 calculations at the DFT-optimized geometries predict that 7-VI is by 56 kJ mol^{-1} (without ZPEC) higher in energy than the most stable one of six-coordinated isomers. The result is consistent with the coordination number of six for the Co^{2+} ion in DMF solution [10,11].

Kamińska-Piotrowicz et al. applied the difference spectra method to extract IR spectral features of DMF affected by $\text{Co}(\text{CF}_3\text{SO}_3)_2$ [18]. They decomposed the ν_{CO} band of the salt-affected spectrum into three components centered at 1648 , 1669 , and 1679 cm^{-1} (Fig. S13b of SM). The 1648 cm^{-1} component was assigned to DMF molecules in the first sphere of Co^{2+} ; the position is consistent with the 1649 cm^{-1} component in our spectra (Fig. 2). The 1669 cm^{-1} component was ascribed to DMF in the second sphere of Co^{2+} . The 1679 cm^{-1} component was attributed to DMF under the influence of CF_3SO_3^- . A quantitative analysis of the spectra suggested that approximately one DMF molecule in the second sphere is affected by the Co^{2+} ion.

In order to examine the effect of Co^{2+} on the ν_{CO} mode of a second-sphere DMF, we investigate six-coordinated isomers of $\text{Co}^{2+}(\text{DMF})_7$. Here, the GD3BJ correction must be indispensable, because the dispersion is significant in the interaction between the first- and second-sphere DMF molecules in stacked geometries. A number of isomers are found; Fig. 6a shows the optimized structure of the most stable isomer (7-I) among them. Other isomers are introduced in section A.3 of SM. In 7-I, the additional DMF molecule is stacked on top

of a first-sphere DMF in 6-I with a mutual orientation similar to that of D-v. Fig. 5d represents the theoretical IR spectrum predicted for 7-I; the spectroscopic data are also tabulated in Table S3 of SM. The spectrum of 7-I is essentially the same as that of 6-I, except one additional mode for each vibration. The highest-frequency ν_{CO} mode of 7-I is predicted at 1685 cm^{-1} , which is due to the in-phase motion of the first-sphere DMF molecules. The next highest-frequency mode emerges at 1669 cm^{-1} . The frequency coincides with the mode of D-v, which is representative of bulk DMF molecules in neat liquid. The 1669 cm^{-1} mode of 7-I involves the nuclear motion of only the second-sphere DMF, while six first-sphere molecules are all stationary during the vibration. All the other ν_{CO} modes of 7-I involve the motion of the first-sphere molecules, while the second-sphere DMF remains stationary. As for the δ_{OCN} vibration, the lowest-frequency mode of 7-I is located at 661 cm^{-1} , which is localized on the second-sphere DMF molecule. All the other modes in the $678\text{--}690\text{ cm}^{-1}$ region are due to the first-sphere molecules.

The analysis of the vibrations of 7-I and other six-coordinated isomers of $\text{Co}^{2+}(\text{DMF})_7$ indicates that the mixing of the ν_{CO} vibrations is rather small between the first- and second-sphere DMF molecules. More importantly, there is a vanishingly small effect of Co^{2+} on the δ_{OCN} and ν_{CO} modes of the second-sphere DMF, as far as the vibrational frequency is concerned.

3.7. Structures and IR spectra of complexes containing both Co^{2+} and ClO_4^-

Kamieńska-Piotrowicz et al. determined the number of DMF molecules in the first sphere of Co^{2+} as a function of the salt concentration. The number was approximately six at the concentrations below 0.3 M but decreased to 4.96 at 0.47 M. Accordingly, it was suggested that the CF_3SO_3^- anion replaced one of the first-sphere molecules and associated with the Co^{2+} ion. Similar ion association might occur in the present system. In order to examine the effect of ion association on the δ_{OCN} and ν_{CO} modes of the first-sphere DMF, we consider the $[\text{Co}(\text{DMF})_5(\text{ClO}_4)_1]^+$ complex. One DMF molecule in 6-I is replaced with the ClO_4^- anion, then the geometry is optimized to obtain CIP-I. Other isomers are explained in

section A.4 of SM. Figs. 6b and 5e show the structure and theoretical IR spectrum of CIP-I, respectively. Spectroscopic data of CIP-I are also collected in Table S3 of SM. The lowest-frequency ν_{CO} mode of CIP-I at 1644 cm^{-1} gains noticeable intensity. The corresponding mode of 6-I is IR inactive because of symmetry, as already noted in section 3.5. Similarly, the highest-frequency mode of CIP-I at 1675 cm^{-1} is much stronger than the corresponding mode of 6-I.

In addition to the complex containing the contact ion pair, we explore the $[\text{Co}(\text{DMF})_6(\text{ClO}_4)_1]^+$ complex, in which the ClO_4^- anion is bound to DMF molecules of $\text{Co}^{2+}(\text{DMF})_6$, forming a solvent-shared ion pair. We find two types of isomers; the details are given in section A.4 of SM. In SSIP-I (Fig. 6c), the ClO_4^- anion binds to three DMF molecules of 6-I simultaneously. In the theoretical IR spectrum of SSIP-I (Fig. 5f), the highest-frequency ν_{CO} mode at 1684 cm^{-1} gains slight intensity, similarly to CIP-I. The 1675 cm^{-1} mode of CIP-I and the 1684 cm^{-1} mode of SSIP-I are higher in frequency than the ν_{CO} mode of the second-sphere DMF in 7-I (1669 cm^{-1}). This point is consistent with the assignment made by Kamińska-Piotrowicz et al. that the highest-frequency (1679 cm^{-1}) component of their spectrum was due to DMF molecules affected by the CF_3SO_3^- anion. They attributed the upshift of the 1679 cm^{-1} component from the band of bulk DMF to the effect of destabilization of the structure of bulk DMF caused by the anion. However, our interpretation is that the upshifts of the 1675 cm^{-1} mode of CIP-I and the 1684 cm^{-1} mode of SSIP-I are a result of the strong coupling among the CO oscillators of the first-sphere DMF molecules, as in the case of 6-I. The role of the anion is that it recovers the IR activity of these modes by breaking the symmetry of 6-I.

Finally, we examine the $\text{Co}(\text{DMF})_5(\text{ClO}_4)_2$ complex, in which one ClO_4^- anion occupies the first sphere of Co^{2+} while the other is bound to first-sphere DMF molecules to form a triple ion pair. Several isomers are found; the details are described in section A.4 of SM. A combination of the configuration of CIP-I and SSIP-I results in TIP-I. Figs. 6d and 5g display the structure and theoretical IR spectrum of TIP-I, respectively. The highest-frequency ν_{CO} mode of TIP-I at 1678 cm^{-1} gains larger intensity than those of CIP-I

and SSIP-I.

In summary, the association of the ClO_4^- anion(s) lowers the structural symmetry around Co^{2+} , which leads to the recovery of the intensity of the IR inactive modes of 6-I and 6-II. The highest- and lowest-frequency ν_{CO} modes of 6-I are examples of such modes. However, the presence of the ClO_4^- anion(s) hardly shifts the δ_{OCN} and ν_{CO} frequencies of the first-sphere DMF molecules. Figs. 5 and S8 with Table 3 of SM demonstrate that, for both δ_{OCN} and ν_{CO} modes, the frequency ranges of the ion pairs are almost the same as those of 6-I and 6-II. In addition, the position of the strongest transition of the ion pairs is close to that of 6-I or 6-II. Accordingly, it is practically difficult to identify the ion pairs from an analysis of the IR spectra in the δ_{OCN} and ν_{CO} regions.

3.8. Formation of ion pairs in DMF solutions

James and Mayes analyzed the symmetric ClO stretch band of ClO_4^- , $\nu_{\text{s}}(\text{ClO})$, in Raman spectroscopy of the $\text{LiClO}_4/\text{DMF}$ system [14]. The band observed at 932 cm^{-1} in a dilute solution was ascribed to free ClO_4^- . In addition to this band, two higher-frequency bands were observed: the first one at 938.5 cm^{-1} for salt concentrations above 1.5 M and the second one at 945 cm^{-1} for solutions above 3 M. The 938.5 cm^{-1} band was attributed to solvent-shared ion pairs, while the 945 cm^{-1} band to contact ion pairs [14].

Now let us look at the triply degenerated asymmetric ClO stretch band of ClO_4^- , $\nu_{\text{as}}(\text{ClO})$, which appears around 1090 cm^{-1} in the IR spectrum. Reproduced in Fig. S11 of SM are the experimental spectra of the neat DMF (Fig. S11b) and 1.0 M solution of $\text{Co}(\text{ClO}_4)_2$ (Fig. S11e). Fig. S11b shows that the in-phase (1064 cm^{-1}) and out-of-phase (1093 cm^{-1}) CH_3 rock (ρ_{CH_3}) modes of DMF are close in frequency to the $\nu_{\text{as}}(\text{ClO})$ modes of ClO_4^- . These three modes are likely to contribute to the broad band observed in the $1040\text{--}1140\text{ cm}^{-1}$ region of the 1.0 M solution. Also represented in Fig. S11 of SM are the theoretical spectra for the $\text{ClO}_4^-(\text{DMF})_4$ complex (Fig. S11e, f), the contact ion pairs (Fig. S11g, h), the solvent-shared ion pairs (Fig. S11i–l), and the triple ion pairs (Fig. S11m, n). As expected, the spectra of the triple ion pairs are a superposition of the spectra of the contact

and solvent-shared ion pairs. The $\nu_{\text{as}}(\text{ClO})$ modes of the solvent-shared ion pairs are located in the range of 1094–1122 cm^{-1} , which fall within the experimental band profile of the 1.0 M solution. In stark contrast, the $\nu_{\text{as}}(\text{ClO})$ modes of the contact ion pairs are located below 1047 cm^{-1} and above 1132 cm^{-1} , which fall outside the experimental profile. The same modes of ClO_4^- unit binding to Co^{2+} in the triple ion pairs are also located outside the experimental profile. A comparison of the experimental and theoretical spectra suggests that the coexistence of the solvent-shared ion pairs is conceivable, but the presence of the contact and triple ion pairs is unlikely.

The left panel of Fig. S11 of SM displays the $\nu_{\text{s}}(\text{ClO})$ region of the theoretical Raman spectra. The $\nu_{\text{s}}(\text{ClO})$ modes of the solvent-shared ion pairs are located in the range of 935–938 cm^{-1} . The $\text{ClO}_4^-(\text{DMF})_4$ complex exhibits the $\nu_{\text{s}}(\text{ClO})$ mode at 938 cm^{-1} . Accordingly, it seems practically impossible to make a distinction between the ion pairs and the unpaired anions from the spectra in the $\nu_{\text{s}}(\text{ClO})$ region.

The CF_3SO_3^- anion has an asymmetrical charge distribution; the dipole moment of the free anion is predicted to be 3.9 D from our MP2 calculations. As a result, the attraction between Co^{2+} and CF_3SO_3^- should be greater than that between Co^{2+} and ClO_4^- . Actually, it was reported that CF_3SO_3^- has higher tendency to form ion pairs [37]. As already noted, Kamińska-Piotrowicz et al. studied $\text{Co}(\text{CF}_3\text{SO}_3)_2$ in DMF and proposed the formation of contact ion pairs at salt concentrations above 0.3 M [18]. In order to assess the proposal, we perform B3LYP-GD3BJ calculations for the $\text{Co}(\text{CF}_3\text{SO}_3)_2/\text{DMF}$ system. The results are provided in section A.5 of SM. In summary, model complexes for contact ion pairs are consistent with the experiment [18] both in the ν_{CO} region of DMF and the SO stretch (ν_{SO}) region of CF_3SO_3^- , except a superfluous ν_{SO} mode predicted at an upshifted frequency.

Dielectric relaxation spectroscopy is sensitive to the formation of weak complexes and has a unique ability to detect and quantify solvent-separated and contact ion pairs in solution. The technique was applied to LiClO_4 , NaClO_4 , $\text{Ba}(\text{ClO}_4)_2$, NaCF_3SO_3 , and $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ in DMF [17,38]. The alkali salts were shown to form solvent-shared ion pairs predominantly [17]. The data for the alkaline-earth salts were not definitive but favored the

presence of solvent-shared ion pairs and double solvent-separated ion pairs [38].

We have shown in this work that vibrational spectroscopy in the δ_{OCN} and ν_{CO} regions of DMF and the $\nu_{\text{as}}(\text{ClO})$ region of ClO_4^- is insufficient to provide definitive evidence for the formation of ion pairs of $\text{Co}(\text{ClO}_4)_2$ dissolved in DMF. Nevertheless, it can be said that, if the ion pairs are present in the solutions, they are likely to be solvent-shared ion pairs rather than contact ion pairs. This point is consistent with the conclusion of dielectric relaxation spectroscopy for the divalent metal ions.

4. Conclusions

Vibrational spectroscopy has been used to investigate the coordination of amide molecules to metal ions. For a particular vibrational mode of amide molecules, spectral features have been decomposed into several components. Some components have been assigned to amide molecules bound to metal ions, while others to molecules free from metal ions. The present calculations demonstrate that such an assignment is valid for the δ_{OCN} vibration of DMF, because there is no overlap of the frequency ranges between the two types of DMF molecules. For the ν_{CO} vibration, on the other hand, the frequency shifts induced by Co^{2+} are smaller than the splitting of the modes by the dipole coupling. As a result, there is an overlap of the frequency ranges between the two types of DMF molecules. The calculations demonstrate that DMF molecules bound to Co^{2+} possibly contribute to the spectral component that has been ascribed to DMF molecules free from Co^{2+} .

The second solvation sphere was revealed for $\text{Co}(\text{CF}_3\text{SO}_3)_2$ dissolved in DMF by means of IR spectroscopy [18]. It was claimed that models of solution employed in preceding vibrational studies were too simple, because the models ignored the second-sphere molecules. The present calculations indicate that there is a vanishingly small effect of Co^{2+} on the δ_{OCN} and ν_{CO} modes of a second-sphere DMF. In addition, the mixing of the nuclear motion is very small between the first- and second-sphere molecules during the δ_{OCN} and ν_{CO} vibrations. In this regard, model complexes without explicit second-sphere molecules are acceptable as a model of Co^{2+} dissolved in DMF.

It was also suggested that the CF_3SO_3^- anion affected the ν_{CO} band in the IR spectrum of DMF [18]. Pairing of the cation and the anion was proposed in the form of a contact ion pair. The calculations show that our model complexes for ion pairs are not in full agreement with the experimental results reported in ref. [18]. For $\text{Co}(\text{ClO}_4)_2$ in DMF, vibrational spectroscopy in the δ_{OCN} and ν_{CO} regions of DMF and the $\nu_{\text{as}}(\text{ClO})$ region of ClO_4^- is insufficient to provide definitive evidence for the formation of ion pairs. It can only be said that the coexistence of the solvent-shared ion pairs is conceivable, but the presence of the contact and triple ion pairs is unlikely.

Declaration of competing interest

There is no conflict of interest.

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Supplementary Data

Supplementary data to this article can be found online at <https://...>

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Figure Captions

Fig. 1. (a, d) ATR-IR spectrum of neat DMF liquid. Theoretical IR spectra of (b, e) DMF dimer D-v in PCM (solvent = DMF) and (c, f) DMF monomer in PCM (solvent = CCl₄). Intensities of weak modes in theoretical spectra are magnified by factors of 2–20. The δ_{OCN} (left) and ν_{CO} (right) regions are expanded in the bottom panels. Dots: experimental points; solid curves: decomposed components.

Fig. 2. ATR-IR spectra in the δ_{OCN} (left) and ν_{CO} (right) regions of (a) neat DMF liquid, (b) 0.3 M, (c) 0.6 M, and (d) 1.0 M solutions of Co(ClO₄)₂ in DMF. Amplitude of all spectra is normalized to have the same maximum height. In the δ_{OCN} region, the intensity is magnified by a factor of 3 after correcting the baseline. Dots: experimental points; solid curves: decomposed components.

Fig. 3. Optimized structures of ClO₄[−](DMF)₄: (a) A-4-I and (b) A-4-II. The ClO₄[−] anion is illustrated by balls and sticks, while DMF molecules by tubes. Theoretical IR spectra of (c) DMF dimer D-v, (d) A-4-I, and (e) A-4-II in the δ_{OCN} (left) and ν_{CO} (right) regions. Dashed curve in (c) reproduces experimental IR spectrum of neat DMF liquid.

Fig. 4. Optimized structures of Co²⁺(DMF)₆: (a) 6-I and (b) 6-II. Top and side views are shown for each isomer. DMF molecules above Co²⁺ are illustrated by balls and sticks, while those below Co²⁺ by tubes.

Fig. 5. Theoretical IR spectra in the δ_{OCN} (left) and ν_{CO} (right) regions of (a) DMF dimer D-v, Co²⁺(DMF)₆: (b) 6-I, (c) 6-II, (d) Co²⁺(DMF)₇: 7-I, (e) [Co(DMF)₅(ClO₄)₁]⁺: CIP-I, (f) [Co(DMF)₆(ClO₄)₁]⁺: SSIP-I, and (g) Co(DMF)₅(ClO₄)₂: TIP-I. Dashed curves in (a) and (b) reproduce experimental IR spectra of neat DMF liquid and 1.0 M solution, respectively.

Fig. 6. Optimized structures of (a) $\text{Co}^{2+}(\text{DMF})_7$: 7-I, (b) $[\text{Co}(\text{DMF})_5(\text{ClO}_4)_1]^+$: CIP-I, (c) $[\text{Co}(\text{DMF})_6(\text{ClO}_4)_1]^+$: SSIP-I, and (d) $\text{Co}(\text{DMF})_5(\text{ClO}_4)_2$: TIP-I. Top and side views are shown for each complex. Second-sphere DMF in 7-I and ClO_4^- units in CIP-I, SSIP-I, and TIP-I are illustrated by balls and sticks, while first-sphere DMF molecules by tubes.

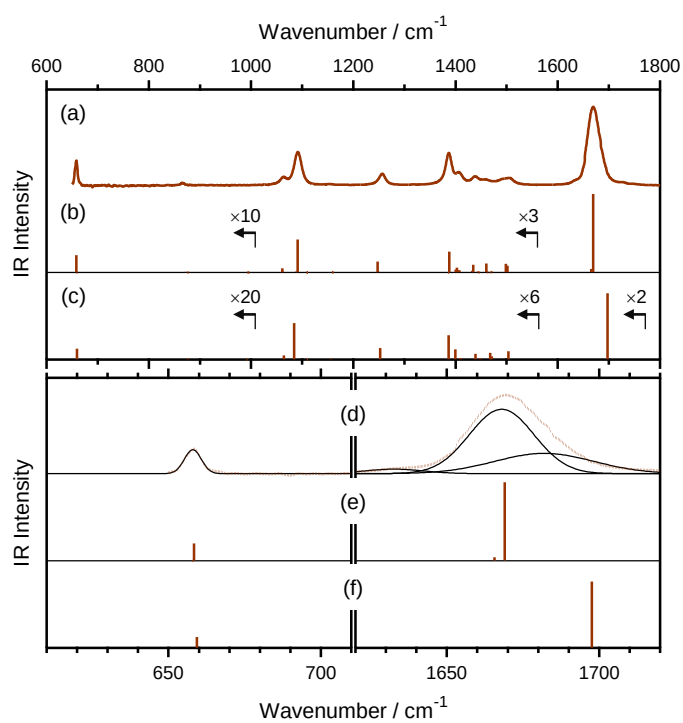


Fig. 1. Ohashi et al.

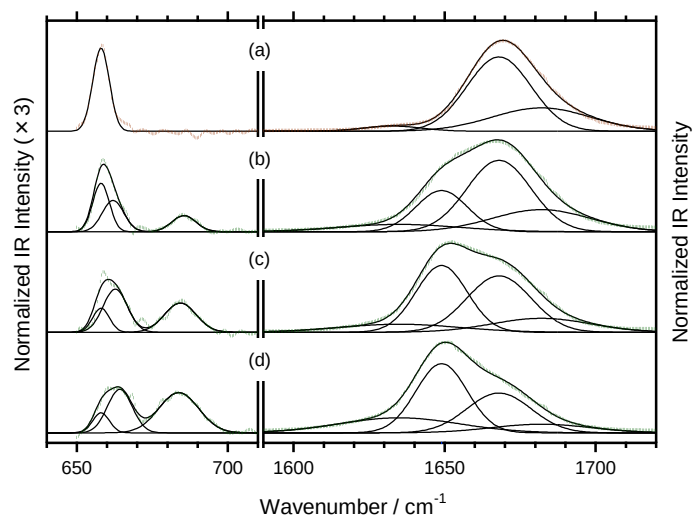


Fig. 2. Ohashi et al.

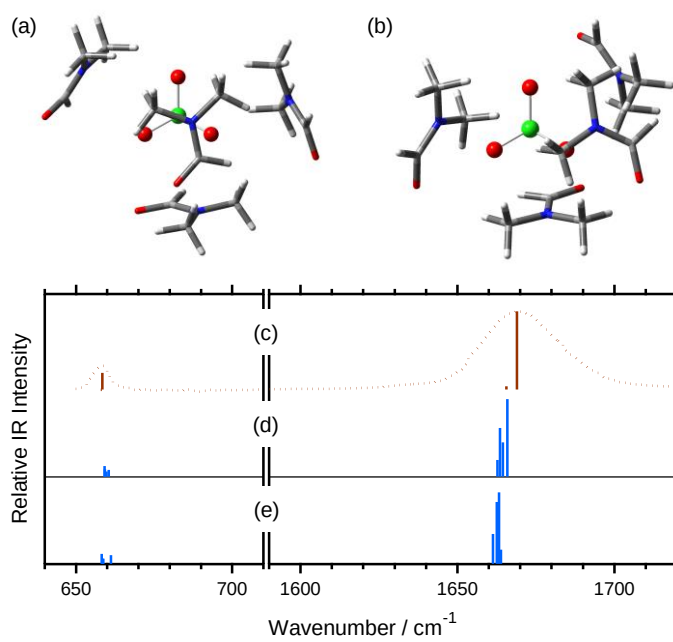


Fig. 3. Ohashi et al.

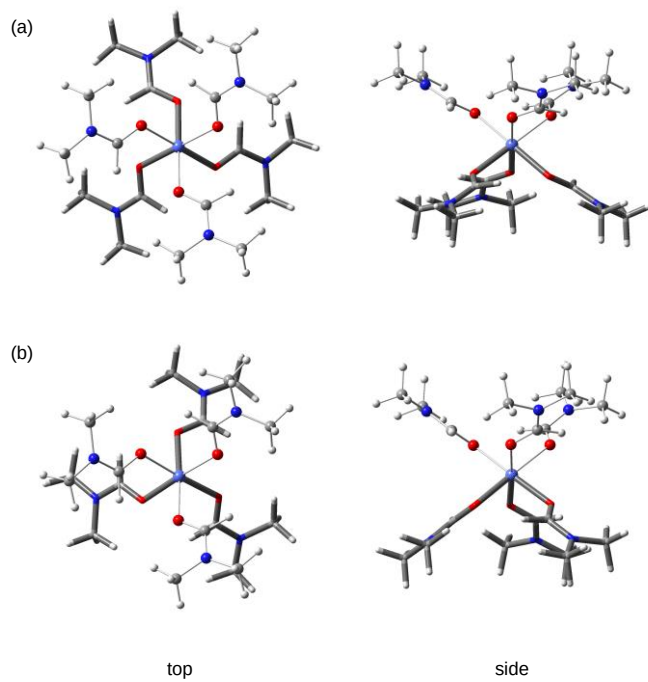


Fig. 4. Ohashi et al.

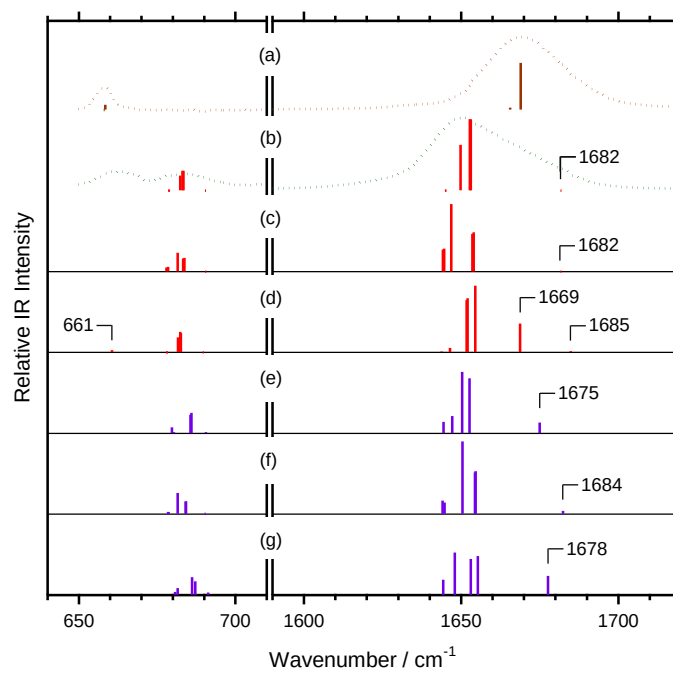


Fig. 5. Ohashi et al.

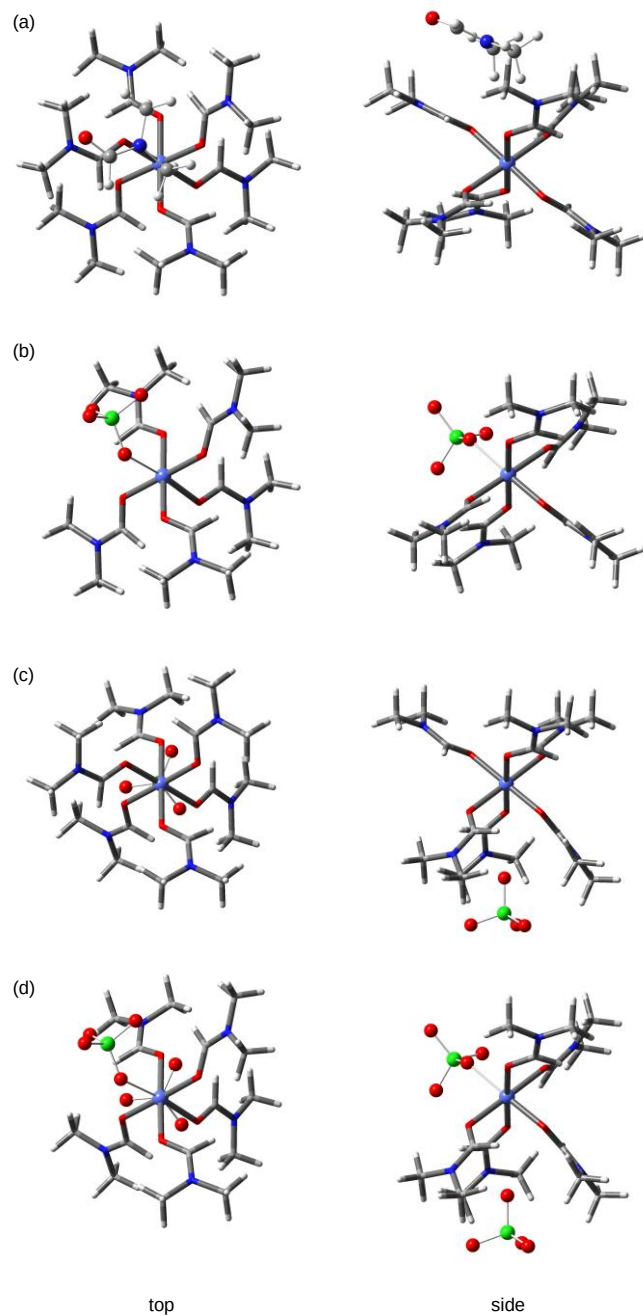


Fig. 6. Ohashi et al.