d-f Metal Ion Interaction through Fe-C ≡ N-Ln Bridge between Dicyanobis(1,10-phenanthroline)iron(II) Complex and $LnCl_3$

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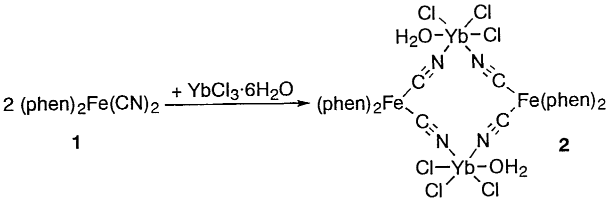
By adding lanthanoid ion (Ln) to a solution of non-charged iron(II) complex, $[Fe(CN)_2(phen)_2]$, the blue shift in MLCT band of the Fe(II) complex was observed in ethanol, but was not in DMSO. The extent of the band shift depends on the lanthanoid ion size, which is explained by means of Fe-C≡N-Ln interaction. In DMSO, however, the lanthanoid ion is solvated too strongly to form the Fe-C≡N-Ln bridging. The existence of the bridging mode was confirmed by means of the crystal analysis for a Fe_2Yb_2 tetranuclear complex.

It has been well known that the solvatochromic complex $[Fe(CN)_2(phen)_2]$ (**1**) acts as a color indicator for acceptor ability of solvent,[1] *i.e.*, the acidity of the solvent. The spectral peak of the complex **1** in solution due to MLCT (t_{2g}→π^*) transition shifts to higher wave number side with increasing in the acceptor number (or acidity) of the solvent.[2,3] On the other hand, lanthanoid ions should have different acidities with their ionic sizes, but there is limited information available on their acidities. The authors expected that the acidity of the lanthanoid ions could be evaluated by d-f metal ion interaction between complex **1** and lanthanoid ion, *i.e.*, Fe-C≡N-Ln bridging. The present communication reports the d-f interaction in solution and the crystal structure of a Fe_2Yb_2 tetranuclear complex, $[Fe_2(CN)_4(phen)_4Yb_2Cl_6(H_2O)_2]\cdot2H_2O\cdot2CH_3OH$ (**2**).



The solvatochromic complex $[Fe(CN)_2(phen)_2]\cdot2H_2O$ was prepared according to the method reported.[4] For spectral measurements, dehydrated **1** and $LnCl_3$ were prepared by drying of $[Fe(CN)_2(phen)_2]\cdot2H_2O$ and $LnCl_3\cdot nH_2O$, respectively, by Abderhalden's dryer at 80 °C for several days. The anhydrous compounds thus obtained were checked by means of IR spectra.

The absorption spectra of the solution (**1**; 1.0×10^{-4} mol dm^{-3}, $LnCl_3$; 1.0×10^{-2} mol dm^{-3}) in ethanol and in DMSO are shown in Figure 1 a and b, respectively. In Figure 1 a, the absorption maximum of the complex **1** is modified gradually depending upon the kind of lanthanoid ion used (without Ln^{3+}; 562, with La^{3+}; 538, with Sm^{3+}; 533, and with Yb^{3+}; 520 nm).[5] That is, the MLCT band of **1** shifts to blue with the decreasing of the ionic size of lanthanoids (lanthanoid contraction) in ethanol solution. Since the decreasing of the ionic size of the lanthanoid ion leads to the increasing of the acidity of the ion, it means that the complex **1** can recognize the acidity as well as the existence of lanthanoid ion. On the other hand, in DMSO which is very strong donor solvent (Figure 1 b), the absorption maximum is 606 nm in each case, and is virtually invariant with existence and the kind of Ln^{3+}.[6] This situation can be interpreted from Figure 2. (a) In weaker donor solvent like ethanol, Ln^{3+} ion can easily interact with the lone-pair of the terminal N atom in Fe-C≡N:, because the ion is solvated by the solvent weakly. (b) In very strong donor solvent like DMSO, Ln^{3+} ion is solvated by the solvent so

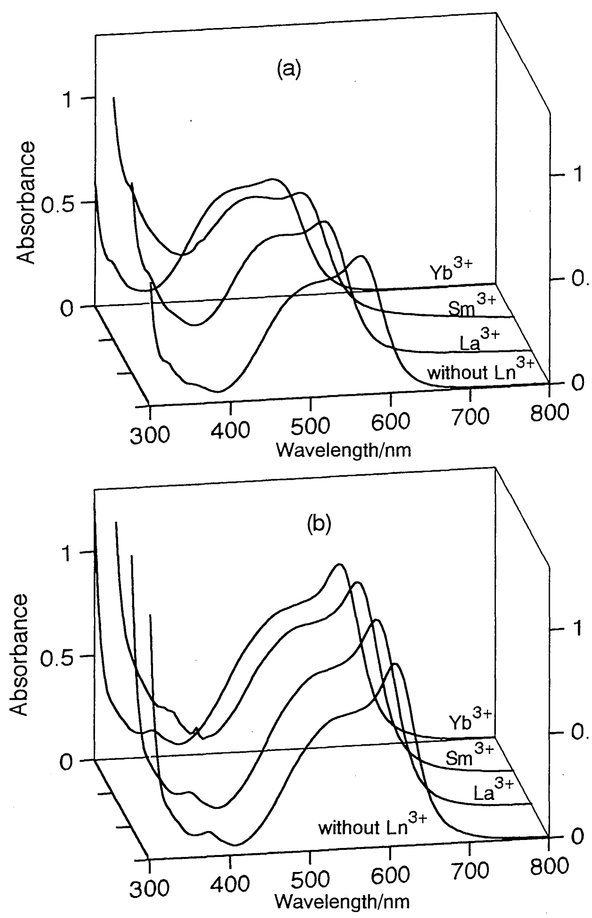


Figure 1. Absorption spectra of **1** with and without Ln^{3+} in ethanol (a) and in DMSO (b).
[1]; 1.0×10^{-4} mol dm^{-3}, [Ln^{3+}]; 1.0×10^{-2} mol dm^{-3}.

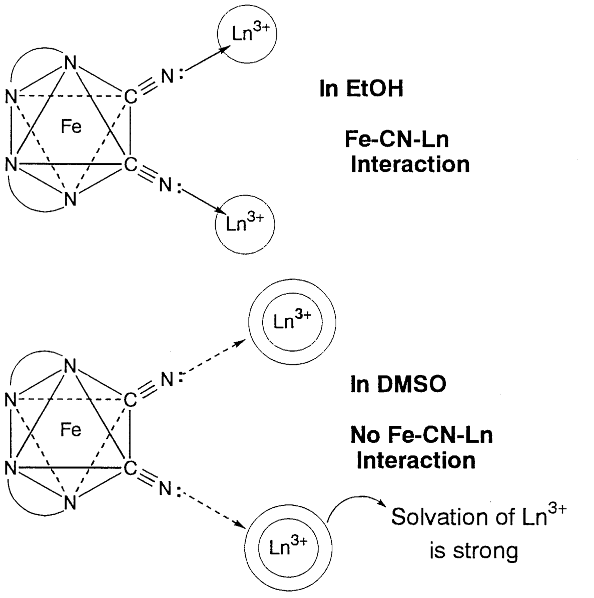


Figure 2. Solvatochromic behavior of d-f metal ion interaction.

strongly that it can interact with the complex **1** no longer.

In order to obtain a direct evidence of the interaction between Ln^{3+} ion and coordinated CN ion in complex **1**, [7] we tried to isolate Fe-Ln mixed metal complexes from alcoholic solutions containing **1** and $LnCl_3$. Actually we have isolated a Fe_2Yb_2 tetranuclear complex **2** from methanolic solution containing **1** and $YbCl_3 \cdot 6H_2O$ as red crystal. The molecular structure of the complex **2** was determined by X-ray crystal analysis, which is shown in Figure 3. From the result, the complex adopts Fe_2Yb_2 tetranuclear structure unit with the -C≡N- bridges which coordinate to Fe and Yb to form the linear bridging. Then the tetranuclear metal ions form a square planar unit. The Yb^{3+} ion is six-coordinated octahedral structure having N_2OCl_3 donor set in which three chloride ions are placed at facial three positions. The Fe(II) coordination structures in the unit are octahedral and very similar to that of the complex **1**.

From these results it can be revealed that the Fe-C≡N-Ln interaction was observed both in solution and in crystal.[8] It is also noteworthy to give the possibility for obtaining polynuclear adducts composed of the non-charged complex **1** and $LnCl_3$.

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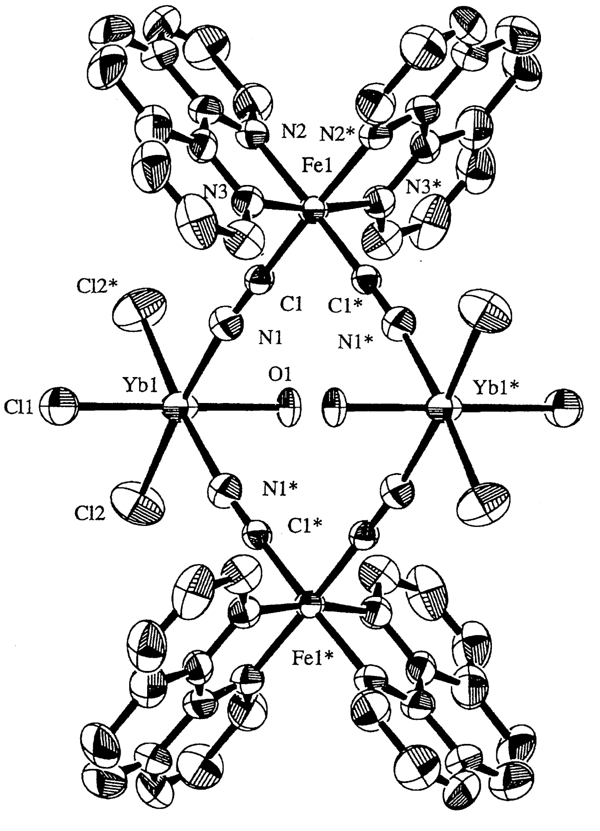

Figure 3. Structure of $[Fe_2(CN)_4(phen)_4Yb_2Cl_6(H_2O)_2]$.[a)]Selected bond distances (Å) and angles (°): Yb-Cl1 2.652(9), Yb-Cl2 2.540(2), Yb-O1 2.20(2), Yb-N1 2.374(7), Fe-N(2) 2.007(7), Fe-N3 1.975(7), Fe-C1 1.860(8), N1-C1 1.163, Cl1-Yb-Cl2 93.8(3), Cl1-Yb-O1 167(1), Cl1-Yb-N1 89.1(4), Cl2-Yb-Cl2* 94.0(1) Cl2-Yb-O1 95.1, Cl2-Yb-N1 175.2(2), Cl2*-Yb-N1 89.6(2), O1-Yb-N1 81.4, N1-Yb-N1* 86.6(3), N2-Fe-N3 82.1(3), N2-Fe-C1 91.8(3), N3-Fe-C1 92.4(3) C1-Fe-C1* 88.6(5), Yb-N1-C1 165.4(7), Fe-C1-N1 179.3(7).

a) Cl(1) and O(1) are disordered each other with occupancy of 1/2.

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5 It was also confirmed that the MLCT band of **1** shifted towards the blue with increase in the concentration of $LnCl_3$ added. For example, the absorption maxima of **1** (1.0×10^{-4} mol dm^{-3}) in ethanol solution with Yb^{3+} are: without Yb^{3+}; 562, $[Yb^{3+}]=1.0\times10^{-4}$; 549, $[Yb^{3+}]=1.0\times10^{-3}$; 529, $[Yb^{3+}]=1.0\times10^{-2}$; 520, and $[Yb^{3+}]=1.0\times10^{-1}$ mol dm^{-3}; 508 nm, respectively.
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7 The crystal data are: $C_{54}H_{48}Cl_6Fe_2N_{12}O_6Yb_2$, *F.W.* = 1627.51, monoclinic, *C*2/m, a = 17.236(1), b = 21.155(1), c = 9.722(1) Å, β = 102.354(7) °, V = 3480.8(5) Å^3, Z = 2, D_m = 1.56, D_c = 1.55 g cm^{-3}, R = 0.047, R_w = 0.043, number of unique reflections = 3382. Elemental Analysis, Found: C, 39.26; H, 3.06; N, 9.96%. Calcd: C, 39.75; H, 2.97; N, 10.30%.
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