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Spectroscopic investigation of a series of sodium lanthanide decatungstates, $\text{Na}_7\text{H}_2\text{Ln(III)}(\text{W}_5\text{O}_{18})_2 \cdot n\text{H}_2\text{O}$ (Ln: La-Yb): the contribution of $4f^n$ electrons to bonding interaction among Ln(III) and polyoxotungstates

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Received 18 August 1995

Abstract

A series of sodium lanthanide decatungstates, $\text{Na}_7\text{H}_2\text{Ln(III)}(\text{W}_5\text{O}_{18})_2 \cdot n\text{H}_2\text{O}$ (Ln = La-Yb) was synthesized and characterized by spectroscopic analyses. The ^{183}W -NMR chemical shifts for the W adjacent to Ln(III) correlated well with the contact parameter in the lanthanide induced shifts, $\langle S_z \rangle$, which had been theorized by Golding. The FT-Raman stretching frequencies for the Ln-O-W bonding also correlated with the theoretical magnetic moments induced from the $4f^n$ electrons in the lanthanide ions in addition to the ionic radii of Ln(III). A direct contribution of the $4f^n$ electrons to the bonding interaction among Ln(III) and the oxotungstates is suggested.

Keywords: Lanthanide decatungstate; ^{183}W -NMR; FT-Raman; $4f^n$ electrons; Bonding interaction

1. Introduction

Lanthanide complexes have been well known as lanthanide shift reagents (LSR) which are quite useful for the interpretation of NMR spectra and the interaction between the metal-ligands, for example see Ref. [1]. It is generally recognized that the observed shifts induced by paramagnetic lanthanide ions (LIS) are a composite of three terms: the contact, the pseudo-contact and the complexation. The last term is usually small and may be estimated from the shifts induced by the diamagnetic lanthanide complexes [2]. For instance, the ^{17}O -NMR chemical shifts in aqueous solution containing Gd(III) ion have been attributed to an electron transfer from the oxygen atom to the Gd(III) ion [3,4]. Golding et al., [5] have successfully interpreted the experimental ^{17}O -NMR results from a second-order perturbation treatment of the calculation of $\langle S_z \rangle$, where bonding effects and spin-orbit coupling

mixing are incorporated. That is, they suggested that the 4f orbitals would not be involved in the direct bonding with the ligands but the bonding would occur primarily through the 6s orbital and the orbital overlap would result in a transfer of the metal electron spin density to the coordinated atoms. Based on Golding's theory, Fedotov et al. conducted a detailed investigation into the ^{17}O -, ^{31}P -, and ^{183}W -NMR of lanthanide complexes from La to Yb with $(\text{PW}_{11}\text{O}_{39})^{7-}$ ligands; $\text{Ln}(\text{PW}_{11}\text{O}_{39})^{11-}$ [6]. In the ^{17}O -NMR of the oxygen ions directly coordinating to Ln(III) and also in the ^{183}W -NMR of the W adjacent to Ln(III), the contact term was found to predominate.

Lanthanide decatungstate anions ($\text{LnW}_{10}\text{O}_{36}^{n-}$; LnW10) have been found to be workable as a catalyst for H_2O_2 oxidation of alcohols to the corresponding carbonyl compounds [7]. In the present paper, the LnW10 compounds through La to Yb were synthesized and characterized by spectrometric analyses such as ICP, FT-IR, FT-Raman and ^{183}W -NMR. Especially, in order to discuss extensively on some contributions of

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4fⁿ electrons to the chemical interaction among Ln(III) and the oxotungstate polyhedron units, the ¹⁸³W-NMR chemical shifts in the W adjacent to Ln(III) and the Ln–O–W stretching bands of the FT-Raman spectra were measured exactly.

2. Experimental details

2.1. Materials and preparation procedures

The reagents used (Special Grade) were all purchased from Kanto Chemical Co. Ltd. A series of LnW10 compounds, sodium salt (Na–LnW10), were prepared generally according to Peacock and Weakley [8]. A typical synthetic procedure is as follows. In LnW10 (Ln: La, Ce, Pr, Sm, Nd, Eu, Gd, Dy, and Ho), Na₂WO₄ · 2H₂O (50 g, 152 mmol) was dissolved in distilled water (100 ml) with stirring, and the pH was adjusted to 7.2 with acetic anhydride. A warm solution of Ln(NO₃)₃ or LnCl₃ · 6H₂O was added dropwise to the hot stirred tungstate solution (90°C). After being vigorously stirred for 15 min, the mixture was filtered and the volume of the filtrate was reduced to ca. 50 ml by evaporating at 60°C. The solution was cooled to 5°C and allowed to stand overnight. The crude crystal obtained was recrystallized three times from warm water. In the case of YbW10, Yb₂O₃ (1.56 g, 3.8 mmol) was dissolved in aqua regia (30 ml) at 80°C, and in the case of ErW10, Er₂(CO₃)₃ · 2H₂O was dissolved in 0.1 mol dm⁻³ solution of HCl. After the Ln-containing solutions were reacted with the tungstate solution and treated in a manner similar to that mentioned above, both Yb- and ErW10 crystals were obtained.

2.2. Instrumental analyses

The compositions of Na, Ln, and W were analyzed by ICP apparatus Simadzu Model ICPS-1000III. The UV spectrum was measured over the range of 210–360 nm using a Shimadzu UV-spectrometer Model UV-120-02. FT-IR spectra were recorded on a Perkin-Elmer Model 1760X over the frequency range of 4000–450 cm⁻¹ with a resolution of 4 cm⁻¹ by the normal KBr-disk method. FT-Raman were recorded on a Nicolet Model Magna 950 over the frequency range of 1200–100 cm⁻¹ with a resolution of 4 cm⁻¹. ¹⁸³W-NMR spectra were obtained on a JEOL GX500 FT-NMR spectrometer operated at 20.8 MHz using 10 mm diameter sample tube at 25°C. In the typical measurement, the concentration was adjusted to more than 0.17 mol dm⁻³ and a 10 μs (ca. 15°) pulse length and 1500–11500 transients were applied. The chemical shifts were measured with respect to 2 mol dm⁻³ of Na₂WO₄ · 2H₂O dissolved in D₂O.

3. Results and discussion

3.1. Characterization of a series of Na₇H₂Ln(III)(W₅O₁₈)₂ (LnW10; Ln = La–Yb)

The sodium salts of LnW10 were prepared and purified as described in the experimental section. The compositions of Na:Ln:W were determined by ICP analyses to be 7:1:10 in all the samples synthesized. The compounds are generally expressed as the formula Na₇H₂LnW₁₀O₃₆ · nH₂O, although the numbers of the water molecules were not determined. In Ln(W₅O₁₈)₂⁹⁻, the Ln(III) ion is square-antiprismatically coordinated by the two units of pentatungstate (W₅O₁₈) with edge-sharing in which four WO₆ octahedron units are bound with edge-sharing in a plane ('belt WO₆') and one WO₆ unit is located at the top of the center of the 'belt WO₆' units with edge-sharing ('cap WO₆'), as reported by Iball et al. [9]. In UV-VIS spectra of the samples, a peak characteristic of LnW10 appeared at ca. 260 nm [10]. The characteristic bands in the FT-IR and FT-Raman spectra compared well with the data of Kazanskii et al. [11]. The FT-Raman spectra for Pr-, Eu-, and DyW10 are illustrated in Fig. 1, as examples of the light, medium, and heavy lanthanide compounds respectively. The strong bands in the 940–970 cm⁻¹ region have been attributed to the W–O–stretching modes and the quite sharp band at ca. 890 cm⁻¹ to the Ln–O–W stretching mode. The big and broad bands in the 200 cm⁻¹ region are usually ascribed to the deformation modes characteristic of such polynuclear oxometalates [12]. The (W–O–W) stretching bands, however, are clearly recognized in the 820–850 and 760–800 cm⁻¹ regions of the FT-IR spectra. The band frequencies for all the samples are summarized in Table 1.

The ¹⁸³W-NMR spectra of those samples were measured as described in the experimental section. The spectra for Pr-, Eu-, and DyW10, for example, are shown in Fig. 2. The quality of the spectrum tended to fall off considerably; that is, the S/N ratio became poor with increasing numbers of 4f electrons (4fⁿ). This might be due to the increase in the paramagnetic moments caused by the 4fⁿ electrons in Ln(III). In fact, a quite clear ¹⁸³W-NMR signal was easily obtained in Y(III)-, La(III)-, and Ce(IV)W10 which have no 4f electrons. Two peaks with the intensity ratio of ca. 4:1 are certainly seen in PrW10, although only roughly in EuW10, and in DyW10 only one peak is seen. The intensive peak should be ascribed to the W in the 'belt WO₆' and the weak one to that in the 'cap WO₆' from the comparison of the intensity ratio. We have never succeeded in detecting either the peak for the 'cap WO₆' in the heavy lanthanide compounds or both peaks in GdW10. The ¹⁸³W-NMR chemical shifts thus observed are also added in Table 1.

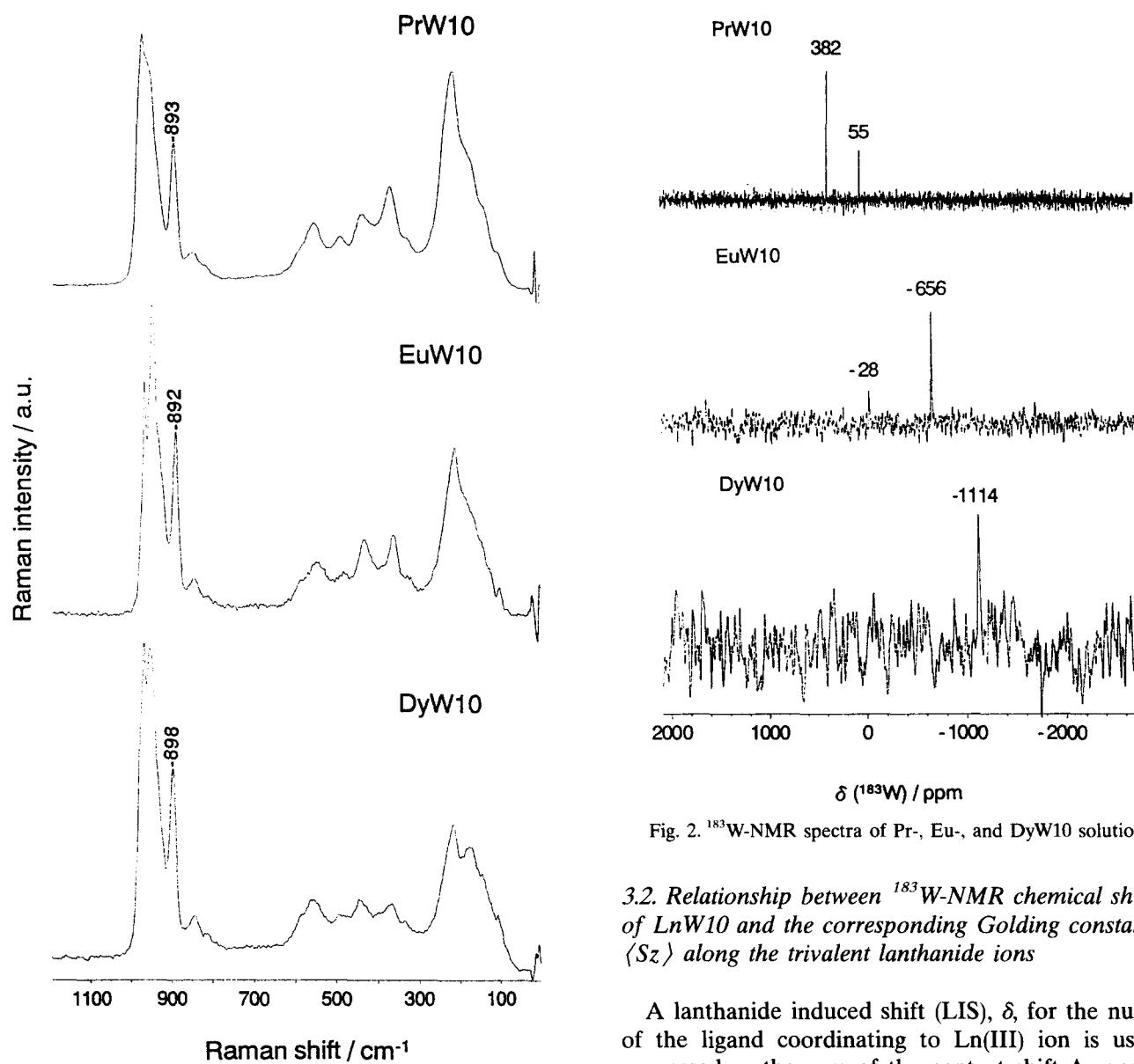
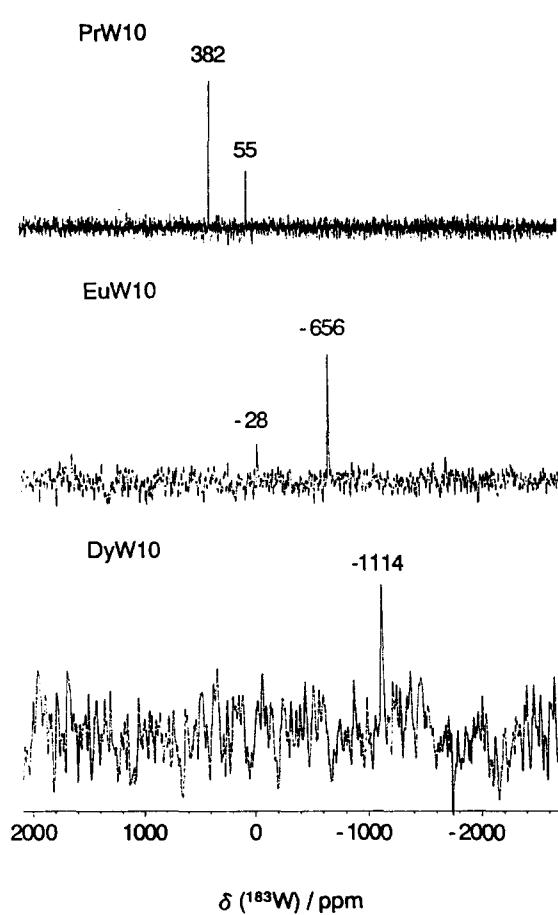


Fig. 1. FT-Raman spectra of Pr-, Eu-, and DyW10 crystals.

Fig. 2. ¹⁸³W-NMR spectra of Pr-, Eu-, and DyW10 solutions.

3.2. Relationship between ¹⁸³W-NMR chemical shifts of LnW10 and the corresponding Golding constant (S_z) along the trivalent lanthanide ions

A lanthanide induced shift (LIS), δ , for the nucleus of the ligand coordinating to Ln(III) ion is usually expressed as the sum of the contact shift Δ_c and the pseudocontact (dipolar) shift Δ_{pc} in Eq. 1 [6].

$$\delta = \Delta_c + \Delta_{pc} = A \langle S_z \rangle / g_N \beta_N + D / r^3 \quad (1)$$

Table 1
Spectroscopic data for a series of sodium lanthanide decatungstate anions

Ln(III)	FT-IR (cm ⁻¹)	FT-Raman (cm ⁻¹)	¹⁸³ W-NMR, δ (ppm)	
			'cap WO ₆ '	'belt WO ₆ '
La	948, 844, 790, 705, 570, 541, 483	969, 946, 889, 842, 548, 482, 434, 365, 322, 209	-19.3	3.5
Ce	933, 849, 799, 703, 579, 548, 487	968, 945, 889, 841, 550, 484, 438, 364, 322, 210	52.4	154.4
Pr	958, 849, 795, 691, 576, 546, 487	969, 893, 847, 553, 488, 435, 369, 215	55	381.6
Nd	953, 850, 801, 696, 577, 546, 485	969, 947, 892, 839, 550, 483, 441, 365, 325, 192	24.9	447.8
Sm	935, 848, 796, 703, 574, 545, 486	957, 893, 846, 547, 486, 435, 368, 327, 214	-25.5	-13.8
Eu	932, 845, 704, 578, 547, 489	969, 949, 892, 849, 545, 484, 435, 367, 332, 328, 216	-28	-655.8
Gd	935, 846, 704, 587, 544, 486	971, 950, 896, 847, 820, 557, 487, 442, 369, 334, 218	—	—
Dy	934, 846, 797, 705, 582, 547, 482	969, 955, 898, 844, 820, 556, 498, 447, 368, 338, 219	—	-1114.2
Ho	956, 853, 790, 694, 581, 549, 488	970, 947, 896, 838, 554, 483, 436, 366, 336, 216	—	-746.9
Er	931, 852, 798, 710, 583, 547, 494	969, 956, 947, 897, 843, 813, 557, 492, 444, 366, 337, 217	—	-319
Yb	936, 834, 793, 711, 587, 552, 492	968, 948, 894, 846, 545, 432, 362, 341, 217	82.6	23.4

where $\langle Sz \rangle$ is the Golding constant, A the hyperfine coupling constant, and the other terms have their usual meanings. As usual, Δ_{pc} predominates in the LIS of atoms further than four bonds away from a paramagnetic ion. The Golding constant $\langle Sz \rangle$ is found from the individual $\langle Sz \rangle_j$ values assuming a Boltzmann distribution. $\langle Sz \rangle_j$ is calculated from the $^{2S+1}L_J$ states in the applied field, in which there is an effect of a mixing of excited states caused by a second-order treatment of spin-orbit coupling interaction (see Ref. [5] in detail).

The contact terms can be regarded as predominating in the present ^{183}W chemical shifts of 'belt WO_6 ' which correspond to the $\text{Ln}-\text{O}-\text{W}$ bonding. Thus, the ^{183}W chemical shifts relisted in Table 2 should be discussed in relation to the parameter $\langle Sz \rangle$. Various $\langle Sz \rangle$ values in Table 1 of Ref. [5] are also listed in Table 2. In Fig. 3 the ^{183}W chemical shifts (Δ) and the $\langle Sz \rangle$ (\circ) with $\gamma = 1$ (column 5), (---) with $\gamma = 0.8-1.1$ (column 7), and (\circ) from a treatment without bonding effects (column 8), where γ denotes the orbital reduction factor (see Ref. [13] in detail), are plotted as a function of the ionic radii r along the lanthanide ions. A better correlation of the experimental (---) is seen in the plots of (Δ) in the light and heavy LnW10 rather than that in the medium LnW10, the plots of which deviate greatly. The ^{183}W -NMR chemical shifts were directly plotted as a function of $\langle Sz \rangle$ in Fig. 4. A good correlation is confirmed except for Eu and Sm which are excluded from the least squares treatment. Such great deviations from the linear line in Eu- and SmW10 would be caused by the fact that the energy differences among the highly excited spectroscopic terms of the $4f^n$ in the anions are not necessarily large relative to kT and thus their mixings result in complexities [14].

This good correlation suggests that the $\text{Ln}-\text{O}$ bond-

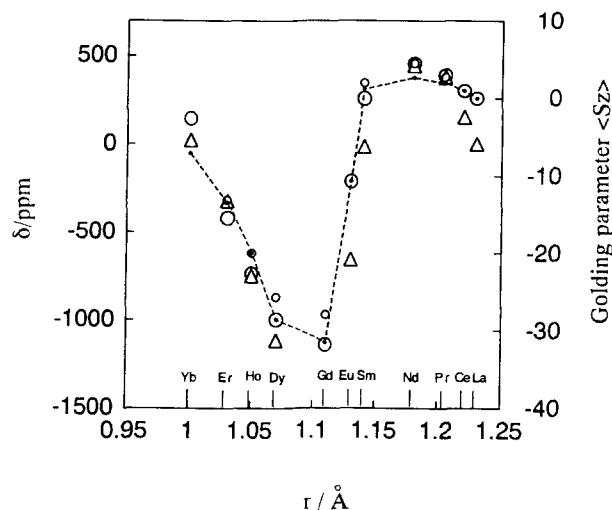


Fig. 3. Plots of the ^{183}W -NMR chemical shifts δ (belt WO_6) in the LnW10 series and the Golding constants $\langle Sz \rangle$ variously evaluated in Ref. [5] (see text) against the ionic radii of Ln(III); correspondence of δ with $\langle Sz \rangle$.

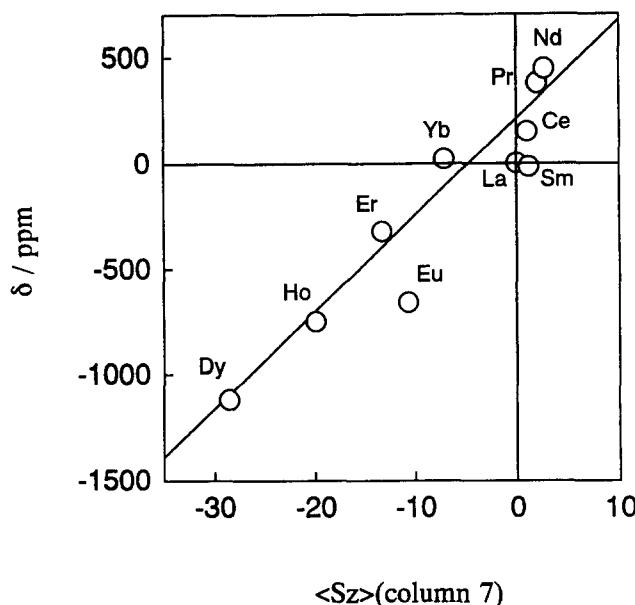
ing will occur primarily through the 6s metal orbital and the orbital overlap will result in a transfer of $4f^n$ -electron spin density to the directly coordinated oxygen ions [5] and further to the W6s orbital through the $\text{Ln}-\text{O}-\text{W}$ bonding. Fedotov et al. [6] precisely investigated the ^{17}O - ^{31}P - and ^{183}W -NMR of lanthanide complexes from La to Yb with $(\text{PW}_{11}\text{O}_{39})^{7-}$ ligands. In the ^{17}O -NMR of the oxygen ions directly coordinating to Ln(III) and also in the ^{183}W -NMR chemical shifts of the W closest to Ln(III), Δ_c was found to predominate. However, the correspondences of the ^{183}W -NMR shifts to the Golding parameters deviated rather greatly along the lanthanide ions, because the situation seemed to be more complicated in their polyanions than the present ones.

Table 2
Correlation of the characteristic FT-Raman band frequency and the ^{183}W -NMR chemical shift of LnW10 with various physicochemical parameters of a series of lanthanide ion and the related compounds, see the text in detail

Ln(III)	f^n	r (\AA)	μ (theor) ^a	$\langle Sz \rangle$ ^b			^{183}W -NMR δ ('belt WO_6) (ppm)	FT-Raman ν ($\text{Ln}-\text{O}-\text{W}$) (cm^{-1})
				column 5	column 7	column 8		
La	f^0	1.23	0	0	0	0	3.5	889
Ce	f^1	1.22	2.54	0.98	0.98	0	154.4	889
Pr	f^2	1.205	3.62	2.97	1.97	2.72	381.6	893
Nd	f^3	1.18	3.68	4.49	2.69	4.49	447.8	892
Sm	f^5	1.14	1.65	-0.06	1.18	1.96	-13.8	893
Eu	f^6	1.13	3.4	-10.68	-10.68	-65.58	-655.8	892
Gd	f^7	1.11	7.98	-31.50	-31.5	-27.99	—	896
Dy	f^9	1.07	10.6	-28.55	-28.55	-25.66	-1114.2	898
Ho	f^{10}	1.05	10.6	-22.63	-19.95	-19.98	-746.9	896
Er	f^{11}	1.03	9.8	-15.37	-13.35	-13.08	-319	897
Yb	f^{13}	1.0	4.5	-2.59	-7.05	—	23.4	894

^a In units of Bohr-magneton per ion.

^b The values were taken from the columns 5, 7, and 8 in Table 1 of Ref. [5].



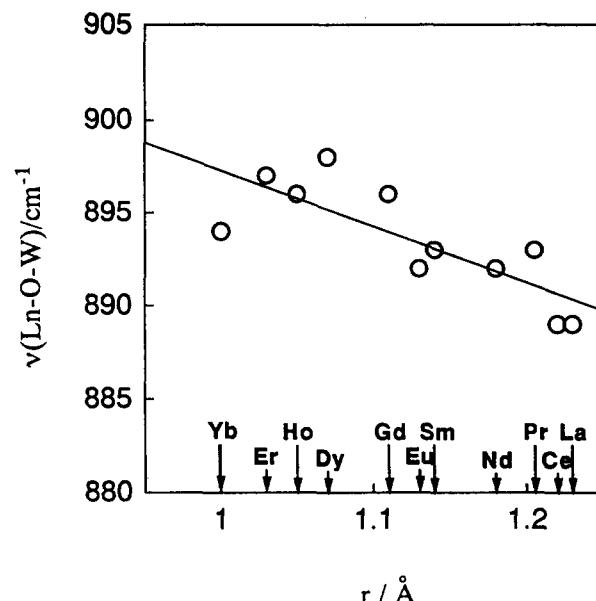
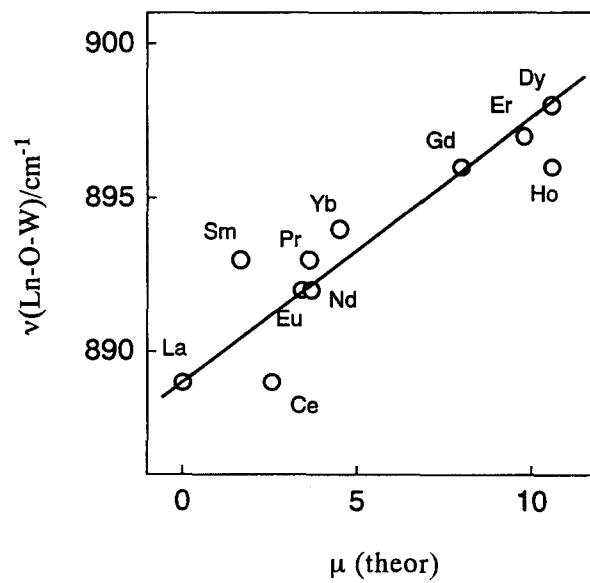
<Sz>(column 7)

Fig. 4. Correlation of δ (belt WO_6) best corresponded to the Golding constants $\langle \text{Sz} \rangle$ (column 7 in Table 2).

3.3. Effects of 4f electrons on bonding interaction between Ln(III) and the polyhedron unit $\text{W}_5\text{O}_{18}^{6-}$

With increasing nuclear charge the 4f orbitals have drastically lowered and thus successive electrons added to the 4f shell are more tightly bound. Consequently, the ionic radii of lanthanide ions (Ln(III)), in general, have became short with increasing atomic number, as shown in Table 2 [15]. Thus, the interaction of Ln(III) with the coordinating polyhedron, $(\text{W}_5\text{O}_{18}^{6-})_2$, may be regarded as varying with the ionic radii of Ln(III) . We first note the remarkably sharp Raman band at ca. 890 cm^{-1} ascribed to the $\text{Ln}-\text{O}-\text{W}$ stretching and thus plotted the wavenumber as a function of the ionic radii, as shown in Fig. 5. The peak roughly tends to shift toward a high wavenumber with increasing atomic number, although the experimental points are considerably diverse, suggesting that the interaction between Ln(III) and the polytungstates becomes strong with the contraction of the ionic radii.

The chemical properties of the compounds containing Ln(III) ion through all 14 lanthanide elements are well known to be remarkably similar, being determined by the 4f shell closed to the $5s^2$ and $5p^6$ outer configuration [16]. In the lanthanide-containing solid compounds, the experimentally determined effective magnetic moments calculated using the Curie–Weiss law are well known to be fairly consistent with the theoretical moments $\mu(\text{theor})$ of Van Vleck and Frank [17] which are listed in Table 2 [16]. The $\text{Ln}-\text{O}-\text{W}$ stretching frequency seems to vary roughly along $\mu(\text{theor})$ in Table 2. In fact, from the direct plots of the wavenumber against $\mu(\text{theor})$, as shown in Fig. 6, a

Fig. 5. Plots of $\nu(\text{Ln}-\text{O}-\text{W})$ Raman band of LnW10 against the ionic radii of Ln(III) .Fig. 6. Correlation of $\nu(\text{Ln}-\text{O}-\text{W})$ to $\mu(\text{theor})$ along LnW10 .

linear correlation, even though it is rough, is confirmed except for a few points. In Eu(III) and Sm(III) , in general, $\mu(\text{theor})$ greatly deviates from that observed with the complexes containing those lanthanide ions for the reasons described above [14]. Consequently, the $\text{Ln}-\text{O}-\text{W}$ stretching frequency, that is, the strength in the bonding between Ln(III) and the $(\text{W}_5\text{O}_{18}^{6-})_2$ is generally mentioned to be varied depending upon not only the ionic radii but also $\mu(\text{theor})$.

In conclusion, it is presented in LnW10 in the lanthanide ions that the ^{183}W -NMR chemical shifts for the W adjacent to Ln correlate well with the Golding

constant $\langle S_z \rangle$, and the FT-Raman stretching frequencies for the Ln–O–W bonding also correlate to the Van Vleck $\mu(\text{theor})$ induced from the $4f^n$ electrons in addition to the ionic radii.

The relation between the contribution of the $4f^n$ electrons to the bonding and the ^{183}W -NMR chemical shifts (LIS) remains an important problem for generally understanding the physicochemical properties of lanthanide compounds.

Acknowledgments

The authors thank Dr. Kohei Kugo (Konan University) for the FT-Raman measurement and also Professor Megumu Munakata (Kinki University) for the ^{183}W -NMR measurement. The authors are grateful to the Ministry of Education, Science and Culture of the Japanese Government for the Grants-in-Aid for Priority Areas 'New Development of Rare Earth Complexes' (No. 06241277).

References

- [1] J.A. Peters, *J. Magn. Reson.*, 68 (1986) 240, and references cited therein.
- [2] R.J.A. Abraham, H.A. Bergen, D.J. Chadwick and F. Sancas-san, *J. Chem. Soc. Chem. Commun.*, (1982) 998.
- [3] (a) L.E. Orgel, *Disc. Faraday Soc.*, 26 (1958) 93; (b) R.G. Shulman and B.J. Wyluda, *J. Chem. Phys.*, 30 (1959) 335.
- [4] W.B. Lewis, J.A. Jackson, J.F. Lemons and H. Taube, *J. Chem. Phys.*, 36 (1962) 694.
- [5] R.M. Golding and M.P. Halton, *Aust. J. Chem.*, 25 (1972) 2577; R.M. Golding and P.Pyykko, *Mol. Phys.*, 26 (1973) 1389.
- [6] M.A. Fedotov, B.Z. Pertsikov and D.K. Danovich, *Polyhedron*, 9 (1990) 1249.
- [7] R. Shiozaki, H. Gotoh and Y. Kera, *Bull. Chem. Soc. Jpn.*, 66 (1993) 2790; R. Shiozaki, H. Kominami and Y. Kera, *Synth. Commun.*, in press.
- [8] R.D. Peacock and T.J.R. Weakley, *J. Chem. Soc. A*, (1971) 1836.
- [9] J. Iball, J.N. Low and T.J.R. Weakley, *J. Chem. Soc., Dalton Trans.*, (1974) 2021.
- [10] K. Nomiya, H. Murasaki and M. Miwa, *Polyhedron*, 4 (1985) 1793.
- [11] L.P. Kazanskii, A.M. Golubev, I.I. Baburina, E.A. Torchenn-kova and V.I. Spitsyn, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1978) 2215.
- [12] C. Rocchicciolini-Deltcheff, R. Thouvenot and M. Fouassier, *Inorg. Chem.*, 21 (1982) 30; C. Rocchicciolini-Deltcheff, M. Fournier and R. Franck, *Inorg. Chem.*, 22 (1983) 207.
- [13] J. Owen and F.H.M. Thornley, *Rep. Prog. Phys.*, 29 (1966) 676; R.M. Golding and T.P. Betteridge, *J. Chem. Phys.*, 51 (1969) 2497.
- [14] C. Kittel, *Introduction to Solid State Physics*, Wiley, 1966, 3rd edn., Chapter 14.
- [15] W.J. Moore, *Physical Chemistry*, Prentice-Hall, 1962, 3rd edn., Chapter 12.
- [16] N.E. Topp, *Chemistry of the Rare-Earth Elements*, Elsevier, 1965, Chapter 1.
- [17] J.H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, London, 1992.