



VARIETY OF STRUCTURES OF BINUCLEAR CHIRAL SCHIFF BASE Ce(III)/Pr(III)/Lu(III)-Ni(II)/Cu(II)/Zn(II) COMPLEXES

Tomoko Hayashi^[a], Haruhiko Shibata^[a], Shingo Orita^[a] and Takashiro Akitsu^{[a]*}

Keywords: Chirality, Schiff base, Ni(II) complex, Cu(II) complex, Zn(II) complex, Lanthanide complex

We have prepared and characterized several 3d-4f (Ni(II), Cu(II) and Zn(II) transition metal (3d) ions and Ce(III), Pr(III), and Lu(III) lanthanide metal (4f) ions) complexes incorporating chiral Schiff base ligands (abbreviated as **CeNi**, **CeCu**, **CeZn**, **PrNi**, **PrCu**, **PrZn**, **LuNi**, **LuCu**, and **LuZn**, respectively). Solid-state CD spectra and diffuse reflectance electronic spectra exhibited reasonable shift by combination of 3d and 4f ions at charge-transfer region. Magnetic features (antiferromagnetic interactions, if any) also exhibited substitution of 3d-4f ions of diamagnetic or paramagnetic spin numbers. Interestingly, determined crystal structures of some of them exhibited different structural characters about coordination numbers, crystalline solvents, and dimetic (or bridging) features nevertheless of 3d-4f metal substitution in identical organic ligands.

* Corresponding Authors

Tel: +81 3 5228 8271; Fax: +81 3 5261 4361

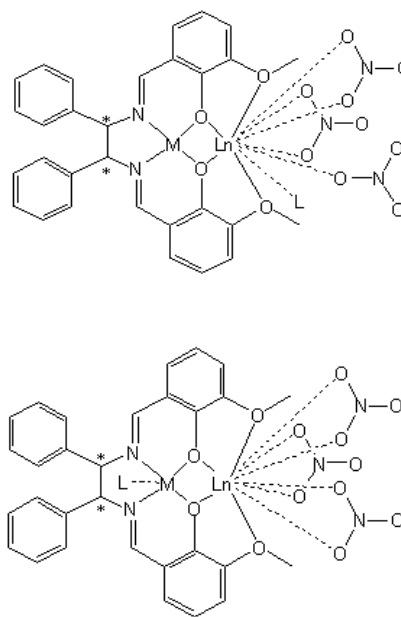
E-Mail: akitsu@rs.kagu.tus.ac.jp

[a] Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Introduction

In recent years, studies on 3d-4f binuclear metal complexes have gained importance with special interest on photophysical properties¹⁻⁴ and magnetic properties⁵⁻¹² arising from interactions between metal ions as well as sole metal ion having suitable electronic states or unpaired electrons. For example, some cyanide-bridged 3d-4f metal complexes¹³⁻¹⁵ have been studied to elucidate empirical estimation of magnetic interaction including paramagnetic ions for understanding multi-functions.¹⁶ In this context, we have been interested in chiral Schiff base 3d-4f dinuclear complexes incorporating so-called salen-type ligands and investigated structure-property correlation and its variety resulting from metal-substitution and their combination.¹⁶⁻¹⁷ By assembling 3d-4f ions, we are interested in characteristic chiroptical properties of the systems involving superexchange magnetic interactions. Generally, systematic comparison of electronic properties for a series of 3d-4f binuclear metal complexes should be carried out for isostructural ones. Indeed many types of 3d-4f binuclear metal complexes take identical crystal structure nevertheless of substitution of relatively small 3d metal ions and relatively large 4f metal ions showing lanthanide contraction typically. In this work, we prepared new chiral Schiff base Ln(III)-M(II) complexes (abbreviated as **CeNi**, **CeCu**, **CeZn**, **PrNi**, **PrCu**, **PrZn**, **LuNi**, **LuCu**, and **LuZn**; Scheme 1) and characterized with electronic spectra, CD spectra, magnetic properties, and X-ray crystallography. In contrast to common series of 3d-4f metal complexes, the present complexes showed drastic changes of crystal structures as well as molecular structures due to not only ionic radii of 4f ions (the smallest Lu(III), middle Pr(III), and the largest Ce(III))

but also coordination environment of 3d ions especially associated with axial ligands.



Scheme 1. Molecular structures of 3d-4f complexes representing different coordination modes of potentially bridging nitrate ligands and axial ligands (L).

Experimental

Materials and Instrumentation

Chemicals of the highest commercial grade available (solvents are from Kanto Chemical, organic compounds are from Tokyo Chemical Industry and metal sources from Wako and Aldrich) were used as received without further purification. Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 2400II CHNS/O analyzer at Tokyo University of Science. Infrared spectra were recorded using KBr pellets on a JASCO FT-IR 4200 plus spectrophotometer equipped with polarizer in the range of

4000-400 cm^{-1} at 298 K. Diffuse reflectance spectra were measured on a JASCO V-570 UV/VIS/NIR spectrophotometer equipped with polarizer in the range of 800-200 nm at 298 K and were converted from absorbance to reflectance by the Kubelka-Munk method. Circular dichroism (CD) spectra were measured as KBr pellets on a JASCO J-820 spectropolarimeter in a range of 800-300 nm at 298 K. Powder X-ray diffraction patterns were also measured by using synchrotron radiation beamtime at KEK PF BL-8B (2010G511) with 8 keV ($\lambda = 1.54184 \text{ \AA}$) with a RIGAKU imaging plate. The $\text{Cu}_{2p_{3/2}}$ and $\text{Cu}_{2p_{1/2}}$ peaks of XAS (soft X-ray absorption spectra) were measured at KEK PF BL-19B (2010G510) under variable temperature. The spectra were corrected by the standard Au sample. The magnetic properties were investigated with a Quantum Design MPMS-XL superconducting quantum interference device magnetometer (SQUID) at an applied field 1000 Oe in a temperature range 2-300 K. Powder samples were measured in a pharmaceutical cellulose capsule. The apparatus signals and the diamagnetic corrections were evaluated from the analogous diamagnetic **LaZn** complex.

X-ray Crystallography

Orange prismatic single crystals of **CeNi**, purple prismatic single crystals of **CeZn**, light-yellow prismatic single crystals of **CeCu**, red prismatic single crystals of **PrNi**, red prismatic single crystals of **LuNi**, brown prismatic single crystals of **LuCu**, and transparent prismatic single crystals of **LuZn** were glued on top of a glass fiber and coated with a thin layer of epoxy resin to measure the diffraction data. Intensity data were collected on a Bruker APEX2 CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data analysis was carried out with a SAINT program package. The structures were solved by direct methods with a SHELXS-97¹⁹ and expanded by Fourier techniques and refined by full-matrix least-squares methods based on F^2 using the program SHELXL-97.¹⁹ A multi-scan absorption correction was applied by a program SADABS. All non-hydrogen atoms were readily located and refined by anisotropic thermal parameters. All hydrogen atoms were located at geometrically calculated positions and refined using riding models.

Crystallographic data for CeNi. $\text{C}_{30}\text{H}_{26}\text{CeNi}_5\text{O}_{13}\text{N}_3\text{O}_9$, crystal size 0.18 mm \times 0.17 mm \times 0.12 mm, $M_w = 863.39$, monoclinic, space group $C2$ (#5), $a = 19.1533(18) \text{ \AA}$, $b = 15.6034(14) \text{ \AA}$, $c = 22.209(2) \text{ \AA}$, $\beta = 99.178(2)^\circ$, $V = 6552.2(11) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 1.750 \text{ Mg m}^{-3}$, $F(000) = 3448$, $R_1 = 0.0542$, $wR_2 = 0.1558$ (20051 reflections), $S = 0.847$, Flack parameter = 0.00(2). (where $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

Crystallographic data for CeCu. $\text{C}_{30}\text{H}_{26}\text{CeCuN}_2\text{O}_4 \cdot \text{CH}_3\text{O}_{10}\text{N}_3$ crystal size 0.13 mm \times 0.10 mm \times 0.07 mm, $M_w = 899.25$, monoclinic, space group $P2_1$ (#4), $a = 10.654(8) \text{ \AA}$, $b = 21.113(16) \text{ \AA}$, $c = 15.715(12) \text{ \AA}$, $\beta = 101.638(11)^\circ$, $V = 3462(5) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.725 \text{ Mg m}^{-3}$, $F(000) = 1796$, $R_1 = 0.0538$, $wR_2 = 0.1631$ (18689 reflections), $S = 0.821$, Flack parameter = -0.02(2). (where $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

Crystallographic data for CeZn. $\text{C}_{30}\text{H}_{26}\text{CeZnN}_2\text{O}_4 \cdot \text{C}_2\text{H}_7\text{O}_{11}\text{N}_3$ crystal size 0.22 mm \times 0.12 mm \times 0.10 mm, $M_w = 933.12$, monoclinic, space group $P2_1$ (#4), $a = 9.3562(9) \text{ \AA}$, $b = 16.1727(15) \text{ \AA}$, $c = 24.001(2) \text{ \AA}$, $\beta = 95.3730(10)^\circ$, $V = 3617.3(6) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.713 \text{ Mg m}^{-3}$, $F(000) = 1872$, $R_1 = 0.0251$, $wR_2 = 0.0794$ (20128 reflections), $S = 0.677$, Flack parameter = -10(10). (where $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

Crystallographic data for PrNi. $\text{C}_{30}\text{H}_{26}\text{PrNiN}_2\text{O}_4 \cdot \text{O}_9\text{N}_3$, crystal size 0.27 mm \times 0.18 mm \times 0.17 mm, $M_w = 864.18$, monoclinic, space group $C2$ (#5), $a = 19.173(2) \text{ \AA}$, $b = 15.6164(18) \text{ \AA}$, $c = 22.193(2) \text{ \AA}$, $\beta = 99.155(2)^\circ$, $V = 6560.4(13) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 1.750 \text{ Mg m}^{-3}$, $F(000) = 3456$, $R_1 = 0.0434$, $wR_2 = 0.0882$ (20321 reflections), $S = 1.012$, Flack parameter = -0.001(13). (where $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

Crystallographic data for LuNi. $\text{C}_{30}\text{H}_{26}\text{LuNiN}_2\text{O}_4 \cdot \text{O}_9\text{N}_3$, crystal size 0.09 mm \times 0.09 mm \times 0.08 mm, $M_w = 898.24$, monoclinic, space group $C2$ (#5), $a = 19.2462(14) \text{ \AA}$, $b = 15.4932(14) \text{ \AA}$, $c = 21.8129(18) \text{ \AA}$, $\beta = 98.9910(10)^\circ$, $V = 6524.4(9) \text{ \AA}^3$, $Z = 8$, $D_{\text{calc}} = 1.857 \text{ Mg m}^{-3}$, $F(000) = 3552$, $R_1 = 0.0315$, $wR_2 = 0.0974$ (17822 reflections), $S = 0.679$, Flack parameter = -0.015(8). (where $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

Crystallographic data for LuCu. $2(\text{C}_{30}\text{H}_{28}\text{LuCuN}_2\text{O}_4 \cdot \text{CH}_3\text{O}_{10}\text{N}_3)\text{CH}_4\text{O}$ crystal size 0.19 mm \times 0.18 mm \times 0.10 mm, $M_w = 1900.25$, triclinic, space group $P1$ (#1), $a = 9.3607(7) \text{ \AA}$, $b = 14.0284(10) \text{ \AA}$, $c = 15.2948(11) \text{ \AA}$, $\alpha = 107.9910(10)^\circ$, $\beta = 104.5540(10)^\circ$, $\gamma = 101.4330(10)^\circ$, $V = 1764.0(2) \text{ \AA}^3$, $Z = 1$, $D_{\text{calc}} = 1.789 \text{ mg/m}^3$, $F(000) = 942$, $R_1 = 0.0193$, $wR_2 = 0.0433$ (9538 reflections), $S = 0.948$, Flack parameter = 0.001(5). (where $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

Crystallographic data for LuZn. $\text{C}_{30}\text{H}_{26}\text{LuZnN}_2\text{O}_4 \cdot \text{O}_9\text{N}_3$ crystal size 0.19 mm \times 0.16 mm \times 0.15 mm, $M_w = 904.90$, monoclinic, space group $P2_1$ (#4), $a = 10.2449(4) \text{ \AA}$, $b = 19.1856(8) \text{ \AA}$, $c = 17.2315(7) \text{ \AA}$, $\beta = 94.8660(10)^\circ$, $V = 3374.7(2) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.781 \text{ Mg m}^{-3}$, $F(000) = 1784$, $R_1 = 0.0410$, $wR_2 = 0.0746$ (20711 reflections), $S = 1.013$, Flack parameter = 0.006(8). (where $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

Preparations

Preparation of CeNi. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL), (*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Nickel(II) acetate tetrahydrate (0.2551 g, 1.00 mmol) was added to the resulting solution to give muddy brown solution of the complex. After stirring at 313 K for 3 h, cerium(III) nitrate hexahydrate

(0.4375 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. After cooling the solution, this orange compound was filtered and recrystallized from methanol/diethyl ether to give orange prismatic single crystals for X-ray analysis.

Yield 0.1288 g (14.92 %). Anal. Found: C, 41.64; H, 2.82; N, 8.05 %. Calc. for $C_{30}H_{26}CeNiN_2O_4 \cdot O_9N_3$: C, 41.33; H, 3.24; N, 8.01 %. IR (KBr cm^{-1}): 669 (s), 694 (s), 735 (s), 774 (s), 846 (s), 945 (s), 1021 (s), 1075 (s), 1168 (s), 1071 (s), 1161 (s), 1231 (s), 1383 (w), 1229 (m), 1292 (m), 1368 (m), 1389 (m), 1458 (m), 1608 (m), 1621 (m) (C=N), 1652 (m), 1700 (m), 2339 (s), 3375 (sh). XRD(2 θ /degree): 7.714, 7.975, 8.700, 9.338, 10.295, 11.31, 11.977, 14.819, 14.848, 16.095, 18.763, 21.025, 21.576, 21.779, 22.765, 23.925, 24.157, 24.650, 26.680, 30.028.

Preparation of CeCu. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL), (*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Copper(II) acetate hydrate (0.2045 g, 1.00 mmol) was added to the resulting solution to give muddy green solution of the complex. After stirring at 313 K for 3 h, cerium(III) nitrate hexahydrate (0.4375 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. After cooling the solution, this purple compound was filtered and recrystallized from methanol/diethyl ether to give crystals containing (nonstoichiometric) CH_4O solvent suitable for X-ray analysis.

Yield 0.5415 g (60.22 %). Anal. Found: C, 41.37; H, 2.83; N, 7.74 %. Calc. for $C_{30}H_{26}CeCuN_2O_4 \cdot CH_3O_{10}N_3$: C, 41.40; H, 3.25; N, 7.79 %. IR (KBr cm^{-1}): 604 (s), 640 (s), 668 (m), 701 (s), 741 (m), 754 (s), 778 (s), 813 (s), 852 (m), 951 (m), 993 (s), 1074 (s), 1097 (s), 1165 (s), 1201 (m), 1240 (s), 1288 (m), 1382 (w), 1448 (m), 1453 (m), 1467 (m), 1490 (m), 1555 (s), 1605 (m), 1626 (m) (C=N), 2353 (s), 2360 (s), 2365 (s), 2425 (s), 3352 (sh). XRD(2 θ /degree): 6.467, 7.743, 9.657, 10.382, 10.962, 11.542, 12.035, 12.644, 12.963, 14.210, 15.022, 15.544, 16.066, 16.385, 17.429, 18.386, 20.097, 20.967, 21.886, 21.982, 23.287, 23.896, 24.969, 25.259, 25.897, 27.144, 28.652, 29.406, 31.146, 32.074, 32.770. XAS: $Cu2p_{3/2}$ 933.3 eV, $Cu2p_{1/2}$ 954.1 eV.

Preparation of CeZn. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL), (*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Zinc(II) acetate tetrahydrate (0.2217 g, 1.00 mmol) was added to the resulting solution to give light-yellow solution of the complex. After stirring at 313 K for 3 h, cerium(III) nitrate hexahydrate (0.4421 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. After cooling the solution, this light-yellow compound was filtered and recrystallized from methanol/diethyl ether to give light-yellow prismatic single crystals containing (nonstoichiometric) CH_4O solvent suitable for X-ray analysis.

Yield 0.3279 g (35.75 %). Anal. Found: C, 39.85; H, 2.90; N, 7.47 %. Calc. for $C_{30}H_{26}CeN_2O_4 \cdot Zn \cdot CH_3O_{10}N_3$: C, 41.91; H, 3.63; N, 7.77 %. IR (KBr cm^{-1}): 545 (s), 624 (s), 641 (s), 667 (m), 700 (s), 740 (m), 753 (s), 765 (s), 813 (s), 847 (m), 962 (m), 977 (m), 1025 (s), 1072 (m), 1094 (m), 1167 (s), 1219 (m), 1226 (m), 1275 (m), 1316 (m), 1382 (w), 1438 (m), 1449 (m), 1457 (m), 1479 (m), 1554 (m), 1605 (m), 1627 (m) (C=N), 1700 (m), 2357 (s), 2422 (s), 3359 (sh). XRD(2 θ /degree): 6.438, 7.772, 9.773, 10.237, 11.049, 12.876, 14.181, 15.689, 16.414, 18.270, 20.300, 24.070, 25.027, 25.230, 25.600, 32.016.

Preparation of PrNi. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL), (*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Nickel(II) acetate tetrahydrate (0.2506 g, 1.00 mmol) was added to the resulting solution to give muddy brown solution of the complex. After stirring at 313 K for 3 h, praseodym(III) nitrate hexahydrate (0.4480 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. After cooling the solution, this orange compound was filtered and recrystallized from methanol/diethyl ether to give crystals for X-ray analysis.

Yield 0.3424 g (39.62 %). Anal. Found: C, 41.38; H, 3.20; N, 7.73 %. Calc. for $C_{30}H_{26}PrNiN_2O_4 \cdot O_9N_3$: C, 41.70; H, 3.03; N, 8.10 %. IR (KBr cm^{-1}): 667 (m), 693 (s), 734 (s), 775 (s), 801 (s), 857 (s), 951 (s), 1021 (s), 1074 (s), 1171 (s), 1233 (m), 1242 (m), 1290 (m), 1383 (m), 1456 (m), 1486 (m), 1557 (m), 1616 (m) (C=N), 1652 (m), 1700 (m), 2330 (s), 2352 (s), 3386 (sh). XRD(2 θ /degree): 7.337, 8.004, 8.729, 9.367, 10.324, 11.339, 12.035, 13.311, 13.291, 14.848, 15.138, 16.124, 16.153, 16.588, 17.0342, 17.516, 18.270, 18.821, 19.952, 22.765, 23.954, 24.186, 24.679, 26.738, 26.796, 27.985, 28.391, 28.971, 29.899, 30.305.

Preparation of PrCu. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL), (*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Copper(II) acetate hydrate (0.1999 g, 1.00 mmol) was added to the resulting solution to give muddy green solution of the complex. After stirring at 313 K for 3 h, praseodym (III) nitrate hexahydrate (0.4505 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. After cooling the solution, this purple compound was filtered and recrystallized from methanol/diethyl ether to give purple prismatic single crystals containing (nonstoichiometric) CH_4O solvent suitable for X-ray analysis.

Yield 0.6473 g (72.19 %). Anal. Found: C, 41.72; H, 3.05; N, 8.09 %. Calc. for $C_{30}H_{26}PrCuN_2O_4 \cdot CH_3O_{10}N_3$: C, 41.37; H, 3.25; N, 7.78 %. IR (KBr cm^{-1}): 642 (s), 668 (m), 698 (s), 739 (m), 809 (s), 852 (s), 961 (s), 977 (s), 993 (s), 1019 (s), 1072 (s), 1095 (s), 1166 (s), 1222 (m), 1227 (s), 1289 (m), 1383 (w), 1454 (m), 1471 (m), 1491 (s), 1557 (s), 1605 (m), 1623 (m) (C=N), 1652 (m), 1700 (m), 2336 (m), 2357 (m), 3386 (sh). XRD(2 θ /degree):

6.467, 7.859, 9.850, 10.295, 11.107, 12.963, 14.268, 15.747, 18.386, 20.445, 21.157, 23.084, 23.519, 23.925, 24.331, 25.201, 25.346, 26.216, 26.825, 27.318, 32.729. XAS: $Cu2p_{3/2}$ 930.9 eV, $Cu2p_{1/2}$ 952.7 eV.

Preparation of PrZn. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL), (*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Zinc(II) acetate tetrahydrate (0.2211 g, 1.00 mmol) was added to the resulting solution to give light-yellow solution of the complex. After stirring at 313 K for 3 h, praseodym (III) nitrate hexahydrate (0.4492 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. After cooling the solution, this light-yellow compound was filtered and recrystallized from methanol/diethyl ether to give light-yellow prismatic single crystals containing (nonstoichiometric) CH_4O solvent suitable for X-ray analysis.

Yield 0.4836 g (53.61 %). Anal. Found: C, 41.26; H, 3.29; N, 7.81 %. Calc. for $C_{30}H_{26}PrN_2O_4Zn.CH_3O_{10}N_3$: C, 41.37; H, 3.25; N, 7.78 %. IR (KBr cm^{-1}): 641 (s), 667 (w), 699 (s), 739 (m), 756 (s), 781 (s), 809 (s), 848 (m), 960 (s), 976 (s), 1024 (s), 1071 (s), 1094 (s), 1168 (s), 1219 (m), 1226 (s), 1285 (m), 1309 (s), 1383 (w), 1419 (s), 1436 (m), 1456 (m), 1471 (m), 1506 (m), 1522 (s), 1567(s), 1623 (m) (C=N), 1652 (m), 1700 (s), 2328 (s), 2360 (s), 3392 (sh). XRD(2θ /degree): 6.409, 7.801, 9.744, 10.208, 10.991, 12.847, 14.123, 15.254, 15.602, 18.212, 19.343, 20.242, 21.025, 22.272, 22.881, 23.316, 23.722, 24.099, 24.477, 24.969, 25.114, 26.013, 26.564, 27.057, 27.521, 28.478, 21.319, 30.769, 31.320, 32.323, 32.509.

Preparation of LuNi. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL), (*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Nickel(II) acetate tetrahydrate (0.2545 g, 1.00 mmol) was added to the resulting solution to give muddy brown solution of the complex. After stirring at 313 K for 3 h, lutetium(III) nitrate hexahydrate (0.3642 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. After cooling the solution, this orange compound was filtered and recrystallized from methanol/diethyl ether to give crystals.

Yield 0.4921 g (54.85 %). Anal. Found: C, 40.14; H, 2.92; N, 7.75 %. Calc. for $C_{30}H_{26}LuNiN_2O_4.O_9N_3$: C, 40.12; H, 3.02; N, 7.80 %. IR (KBr cm^{-1}): 583 (s), 591 (s), 667 (m), 695 (m), 736 (m), 779 (s), 809 (s), 863 (s), 952 (s), 1025 (m), 1073 (m), 1171 (s), 1231 (m), 1275 (m), 1314 (m), 1383 (w), 1440 (m), 1474 (m), 1506 (m), 1559 (m), 1610 (m), 1619 (m) (C=N), 1700 (s), 2328 (s), 2922 (s), 3390 (sh). XRD(2θ /degree): 7.377, 8.062, 8.758, 9.388, 10.440, 11.426, 12.093, 13.340, 13.688, 14.065, 14.906, 15.109, 16.240, 16.385, 16.762, 17.574, 18.357, 18.734, 20.157, 21.199, 21.605, 21.808, 22.852, 23.896, 24.218, 24.302, 25.056, 26.709, 28.275, 30.044, 30.218, 30.450, 31.378.

Preparation of LuCu. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL),

(*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Copper(II) acetate hydrate (0.2027 g, 1.00 mmol) was added to the resulting solution to give muddy green solution of the complex. After stirring at 313 K for 3 h, lutetium(III) nitrate hexahydrate (0.3610 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. The solution was evaporated under reduced pressure, and deep brown compound was yielded. This compound was filtered and recrystallized from methanol/diethyl ether to give crystals containing (nonstoichiometric) CH_4O solvent suitable for X-ray analysis.

Yield 0.2852 g (30.54 %). Anal. Found: C, 39.74; H, 3.22; N, 7.53 %. Calc. for $C_{30}H_{26}LuCuN_2O_4.CH_3O_{10}N_3$: C, 39.86; H, 3.13; N, 7.74 %. IR (KBr cm^{-1}): 649 (s), 667 (w), 698 (m), 742 (m), 854 (s), 955 (s), 1020 (s), 1071 (s), 1093 (s), 1167 (s), 1220 (m), 1239 (s), 1288 (m), 1383 (w), 1464 (m), 1495 (s), 1533 (s), 1557 (s), 1605 (m), 1623 (m) (C=N), 1652 (s), 1700 (m), 2345 (s), 3344 (sh). XRD(2θ /degree): 6.264, 6.641, 6.699, 7.192, 7.656, 8.236, 9.309, 9.628, 10.237, 10.759, 11.194, 11.803, 12.209, 12.644, 12.934, 13.253, 13.746, 14.355, 15.283, 16.414, 17.023, 18.647, 18.821, 20.184, 21.866, 22.678, 24.447, 24.940, 25.752, 26.245, 27.144, 27.666, 29.000, 30.305, 30.943, 32.074. XAS: $Cu2p_{3/2}$ 933.5 eV, $Cu2p_{1/2}$ 954.1 eV.

Preparation of LuZn. To a solution of *o*-vanillin (0.305 g, 2.00 mmol) dissolved in methanol (60 mL), (*1R,2R*)-(+)-1,2-diphenylethylenediamine (0.212 g, 1.00 mmol) was added and stirred at 313 K for 2 h to give a ligand. Zinc(II) acetate tetrahydrate (0.2243 g, 1.00 mmol) was added to the resulting solution to give light-yellow solution of the complex. After stirring at 313 K for 3 h, lutetium(III) nitrate hexahydrate (0.3526 g 1.00 mmol) was added to the resulting solution and the reaction was refluxed for 4 h at 373 K. The solution was evaporated under reduced pressure, and yellow compound was yielded. This compound was filtered and recrystallized from methanol/diethyl ether to give crystals containing (nonstoichiometric) CH_4O solvent suitable for X-ray analysis.

Yield 0.5046 g (53.91 %). Anal. Found: C, 39.74; H, 3.12; N, 7.57 %. Calc. for $C_{30}H_{26}LuN_2O_4Zn.CH_3O_{10}N_3$: C, 39.78; H, 3.12; N, 7.48 %. IR (KBr cm^{-1}): 507 (s), 525 (s), 543 (s), 592 (s), 640 (s), 667 (m), 700 (m), 740 (m), 771 (s), 809 (s), 851 (m), 959 (m), 974 (m), 1024 (s), 1071 (m), 1092 (m), 1165 (m), 1219 (m), 1285 (m), 1382 (w), 1452 (m), 1470 (m), 1557 (s), 1623 (m) (C=N), 1652 (m), 1700 (m), 2424 (s), 3340 (sh). XRD(2θ /degree): 6.206, 7.308, 9.309, 10.005, 11.165, 11.600, 13.195, 14.616, 18.937, 19.169, 21.895, 22.881, 29.58.

Results and Discussion

Solid-state CD and electronic spectra

Figures 1, 2, and 3 show diffuse reflectance electronic spectra and CD (circular dichroism) spectra of Ce-complexes (**CeNi**, **CeCu**, and **CeZn**), Pr-complexes (**PrNi**, **PrCu**, and **PrZn**), and Lu-complexes (**LuNi**,

LuCu, and **LuZn**), respectively. For Ce-complexes, d-d bands (of Ni(II) or Cu(II) moieties) of electronic spectra appeared at about 18300-18600 cm^{-1} , while the corresponding d-d and CT (charge transfer) bands of CD spectra appeared at about 16200-17400 cm^{-1} and 24100-25100 cm^{-1} , respectively. For Pr-complexes, d-d bands (of Ni(II) or Cu(II) moieties) of electronic spectra appeared at about 18300-18400 cm^{-1} , while the corresponding d-d and CT bands of CD spectra appeared at about 16200-17400 cm^{-1} and 24100-25100 cm^{-1} , respectively. For Lu-complexes, d-d bands (of Ni(II) or Cu(II) moieties) of electronic spectra appeared at about 18700-19000 cm^{-1} , while the corresponding d-d and CT bands of CD spectra appeared at about 16000-16300 cm^{-1} and 23300-27100 cm^{-1} , respectively. Therefore, spectral changes, in particular charge transfer bands,¹⁷ are attributed to substitution and/or coordination environment of 3d metal ions.

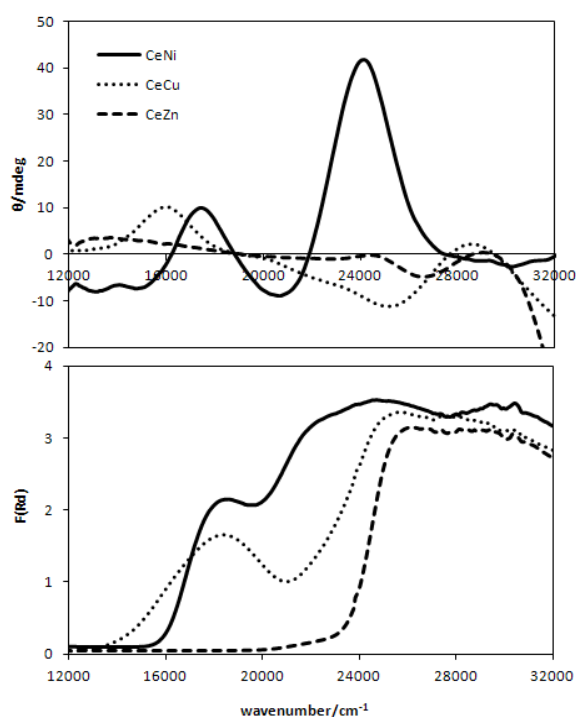


Figure 1. Solid-state CD and diffuse reflectance electronic spectra of **CeNi**, **CeCu**, and **CeZn**.

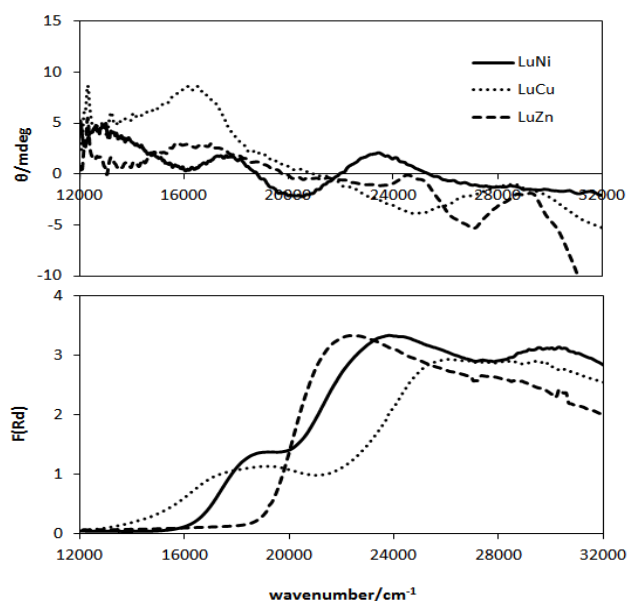
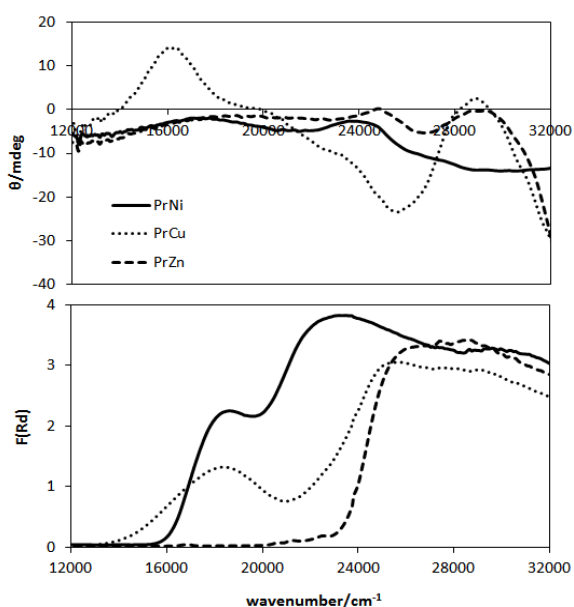


Figure 2. Solid-state CD and diffuse reflectance electronic spectra of **PrNi**, **PrCu**, and **PrZn**.

Figure 3. Solid-state CD and diffuse reflectance electronic spectra of **LuNi**, **LuCu**, and **LuZn**.

Magnetic properties

Figures 4, 5, 6 show the χ_{MT} vs T plots for Ce-complexes (**CeNi**, **CeCu**, and **CeZn**), Pr-complexes (**PrNi**, **PrCu**, and **PrZn**), and Lu-complexes (**LuNi**, **LuCu**, and **LuZn**), respectively. For 3d metal ions, Ni(II) ($3d^8$) and Zn(II) ($3d^{10}$) ions are diamagnetic ($S = 0$) and Cu(II) ($3d^9$) ion is paramagnetic ($S = 1/2$), while for 4f metal ions, Ce(III) ($4f^1$), Pr(III) ($4f^2$), and Lu(III) ($4f^{14}$) ions are $S = 1/2$, 1, and 0, respectively. Generally, 4-coordinated square planar and 6-coordinated octahedral Ni(II) complexes exhibit diamagnetism and paramagnetism, respectively, while 5-coordinated square pyramidal ones is not clear. Paramagnetism of Ni(II) ion is in accordance with coordination geometries as their metal complexes. That valence and spin state of Cu(II) ion is kept under the experimental conditions was also supported by the results of XAS. In this way, magnetic interaction between 3d and 4f ions can potentially be observed only for **CeCu** and **PrCu** composed of two paramagnetic ions.

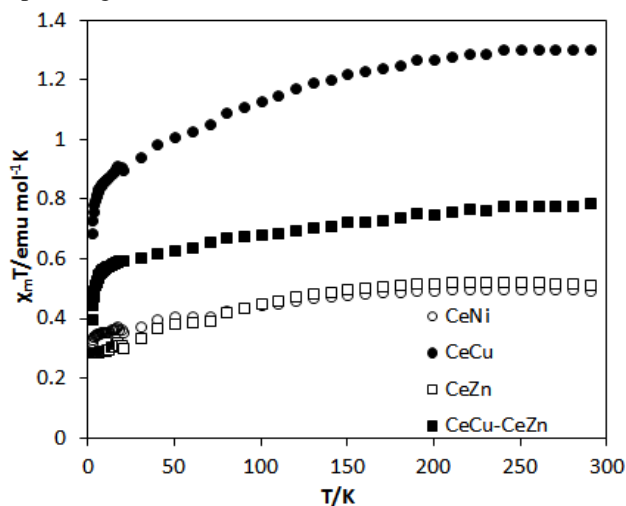
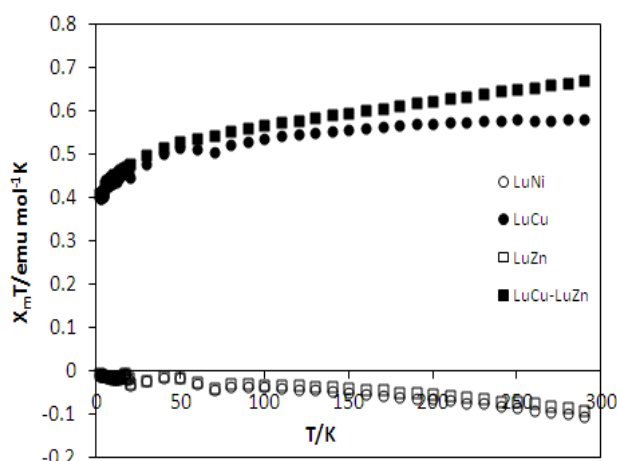
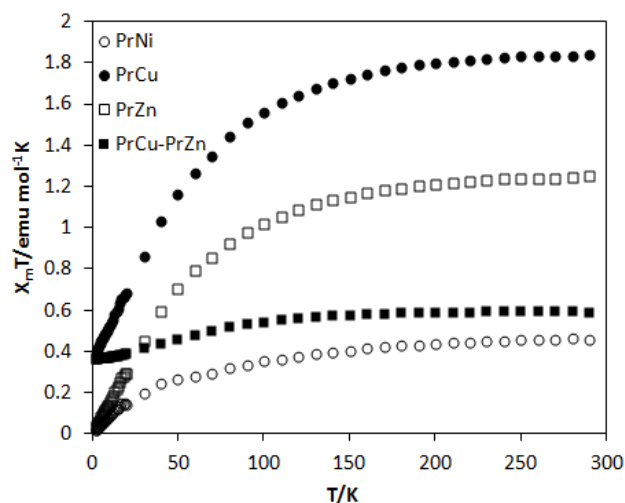


Figure 4. The $\chi_M T$ vs T plots for **CeNi**, **CeCu**, and **CeZn**.**Figure 5.** The $\chi_M T$ vs T plots for **PrNi**, **PrCu**, and **PrZn**.**Figure 6.** The $\chi_M T$ vs T plots for **LuNi**, **LuCu**, and **LuZn**.

By comparing with the corresponding paramagnetic 4f and diamagnetic 3d complexes, namely **CeZn** for **CeCu** and **PrZn** for **PrCu**, and evaluating the differences of $\chi_M T$ values, these superexchange interactions via phenolate oxygen atoms are antiferromagnetic ones. It should be noted that discussion above is mentioned based on structural similarity (not isostructure completely) of 3d ion - phenolate oxygen atoms - 4f ion units for all complexes. Judgement for paramagnetic interactions may be impossible according to the way under this condition.¹⁸

Crystal structures

Crystal structures could be determined for **CeNi**, **CeCu**, **CeZn**, **PrNi**, **LuNi**, **LuCu**, and **LuZn**. According to powder XRD patterns, structural similarity between **LuCu** and **LuZn** and difference to **LuNi** are comparable to the corresponding Pr-complexes. Unfortunately, precise structures of **PrCu** and **PrZn** are not determined. However, one of the three nitrate ions of **CeCu** acts monodentate ligands though XRD patterns are almost

similar to **CeZn**. In this way, structural differences between arbitrary two complexes may be reliable, whereas reliable discussion of structural similarity and detailed structure-property correlation are restricted to comparison with only 7 complexes characterized structurally.

Figure 7 depicts structure of **CeNi**. Ni(II) ion affords a 4-coordinated distorted square planar geometry without methanol ligands and Ce(III) ion affords a 10-coordinated environment with distorted square pyramidal from the plane made by two nitrate ligands. Phenyl groups are located under a salen-plane with $C40-C39-C54-C55 = 166.6(8)$ and $C10-C9-C24-C25 = 156.3(9)^\circ$.

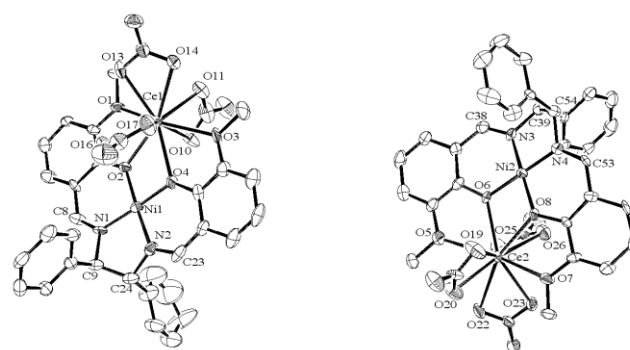


Figure 7. Molecular structures of **CeNi** showing selected atom labeling scheme. Hydrogen atoms are omitted clarity. Selected bond distance (\AA) and bond or torsion angles ($^\circ$): Ni1-N1 = 1.838(9), Ni1-N2 = 1.854(9), Ni1-O2 = 1.844(8), Ni1-O4 = 1.853(8), Ce1-O1 = 2.585(8), Ce1-O2 = 2.485(7), Ce1-O3 = 2.633(8), Ce1-O4 = 2.469(8), Ni2-N3 = 1.823(8), Ni2-N4 = 1.830(9), Ni2-O6 = 1.846(7), Ni2-O8 = 1.846(8), Ce2-O5 = 2.615(8), Ce2-O6 = 2.429(7), Ce2-O7 = 2.612(8), Ce2-O8 = 2.497(7), N1-Ni1-N2 = 86.4(4), O2-Ni1-N1 = 94.7(3), O2-Ni1-N2 = 175.8(3), O2-Ni1-O4 = 84.6(3), O4-Ni1-N1 = 175.2(4), O4-Ni1-N2 = 94.6(4), N3-Ni2-N4 = 85.9(4), O6-Ni2-N3 = 94.8(3), O6-Ni2-N4 = 177.5(3), O6-Ni2-O8 = 84.4(3), O8-Ni2-N3 = 176.9(3), O8-Ni2-N4 = 95.0(3), O1-Ce1-O2 = 60.8(3), O1-Ce1-O3 = 157.4(2), O1-Ce1-O4 = 120.0(3), O2-Ce1-O3 = 120.2(3), O2-Ce1-O4 = 60.3(3), O3-Ce1-O4 = 61.5(3), O5-Ce2-O6 = 61.4(2), O5-Ce2-O7 = 158.9(3), O5-Ce2-O8 = 118.2(3), O6-Ce2-O7 = 120.8(2), O6-Ce2-O8 = 60.4(3), O7-Ce2-O8 = 60.5(3).

Figure 8 depicts structure of **CeCu** of a dimer bridged via a nitrate ligand (see Scheme 1 [up]). Cu(II) ion affords a 4-coordinated almost square planar geometry, and Ce(III) ion affords a 10-coordinated environment with distorted square pyramidal towards a bridging nitrate ligand. Phenyl groups indicate slight distortion with $C40-C39-C54-C55 = 65.8(14)$ and $C25-C24-C9-C10 = 59.2(13)^\circ$. Figure 9 depicts structure of **CeZn**. Zn(II) ion affords a 5-coordinated square pyramidal geometry lifted up towards axial methanol ligands and Ce(III) ion affords a 10-coordinated environment with distorted square pyramidal from the plane made by two nitrate ligands. Phenyl groups connected to asymmetric carbon atoms indicate slight distortion with $C40-C39-C54-C55 = 59.9(4)$ and $C25-C24-C9-C10 = 58.0(4)^\circ$.

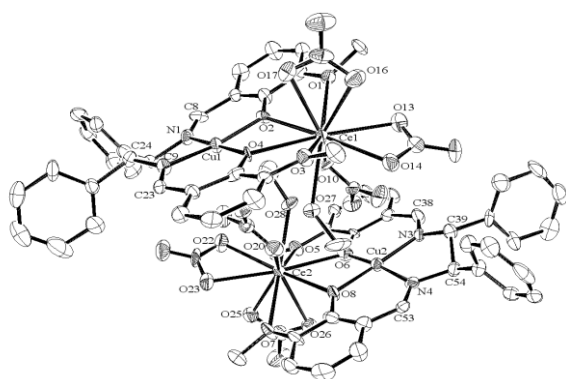
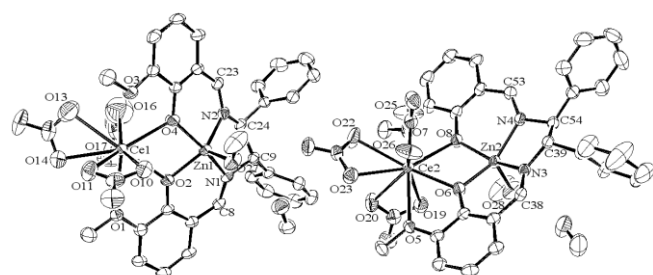


Figure 8. Molecular structures of **CeCu** showing selected atom labeling scheme. Hydrogen atoms are omitted clarity. Selected bond distance (Å) and bond or torsion angles (°): Cu1-N1 = 1.910(10), Cu1-N2 = 1.932(9), Cu1-O2 = 1.897(7), Cu1-O4 = 1.909(8), Ce1-O1 = 2.677(10), Ce1-O2 = 2.453(9), Ce1-O3 = 2.705(9), Ce1-O4 = 2.508(7), Cu2-N3 = 1.928(9), Cu2-N4 = 1.908(11), Cu2-O6 = 1.898(10), Cu2-O8 = 1.908(8), Ce2-O5 = 2.718(9), Ce2-O6 = 2.497(9), Ce2-O7 = 2.693(11), Ce2-O8 = 2.478(9), N1-Cu1-N2 = 85.8(4), O2-Cu1-N1 = 95.8(4), O2-Cu1-N2 = 170.2(4), O2-Cu1-O4 = 83.4(3), O4-Cu1-N1 = 178.9(4), O4-Cu1-O2 = 95.1(4), N3-Cu2-N4 = 86.5(4), O6-Cu2-N3 = 83.3(4), O6-Cu2-N4 = 171.3(4), O6-Cu2-O8 = 83.3(4), O8-Cu2-N3 = 178.1(4), O8-Cu2-N4 = 94.8(4), O1-Ce1-O2 = 59.5(3), O1-Ce1-O3 = 145.9(3), O1-Ce1-O4 = 117.0(3), O2-Ce1-O3 = 118.2(3), O2-Ce1-O4 = 61.4(2), O3-Ce1-O4 = 58.9(3), O5-Ce2-O6 = 59.1(3), O5-Ce2-O7 = 145.5(3), O5-Ce2-O8 = 117.8(3), O6-Ce2-O7 = 117.5(4), O6-



Ce2-O8 = 61.1(3), O7-Ce2-O8 = 60.0(3).

Figure 9. Molecular structures of **CeZn** showing selected atom labeling scheme. Hydrogen atoms are omitted clarity. Selected bond distance (Å) and bond or torsion angles (°): Zn1-N1 = 2.005(3), Zn1-N2 = 2.043(4), Zn1-O2 = 1.997(3), Zn1-O4 = 1.996(3), Ce1-O1 = 2.674(3), Ce1-O2 = 2.408(3), Ce1-O3 = 2.758(3), Ce1-O4 = 2.407(3), Zn2-N3 = 2.053(3), Zn2-N4 = 2.043(3), Zn2-O6 = 2.005(3), Zn2-O8 = 1.975(3), Ce2-O5 = 2.678(3), Ce2-O6 = 2.428(3), Ce2-O7 = 2.681(4), Ce2-O8 = 2.432(3), N1-Zn1-N2 = 83.21(14), O2-Zn1-N1 = 92.21(13), O2-Zn1-N2 = 141.52(14), O2-Zn1-O4 = 80.89(11), O4-Zn1-N1 = 160.41(14), O4-Zn1-O2 = 90.81(12), N3-Zn2-N4 = 81.81(13), O6-Zn2-N3 = 90.29(13), O6-Zn2-N4 = 149.33(14), O6-Zn2-O8 = 80.67(11), O8-Zn2-N3 = 149.26(14), O8-Zn2-N4 = 91.11(12), O1-Ce1-O2 = 60.43(9), O1-Ce1-O3 = 152.3(1), O1-Ce1-O4 = 123.82(9), O2-Ce1-O3 = 121.0(1), O2-Ce1-O4 = 65.09(9), O3-Ce1-O4 = 58.4(1), O5-Ce2-O6 = 59.87(9), O5-Ce2-O7 = 154.33(12), O5-Ce2-O8 = 122.34(8), O6-Ce2-O7 = 121.76(10), O6-Ce2-O8 = 64.03(9), O7-Ce2-O8 = 59.74(10).

Figure 10 depicts structure of **PrNi**. Ni(II) ion affords a 4-coordinated distorted square planar geometry without methanol ligands and Pr(III) ion affords a 10-coordinated environment with distorted square pyramidal from the

plane made by two nitrate ligands. Phenyl groups are located under a salen-plane with C40-C39-C54-C55 = 154.1(5) and C10-C9-C24-C25 = 165.6(5) °.

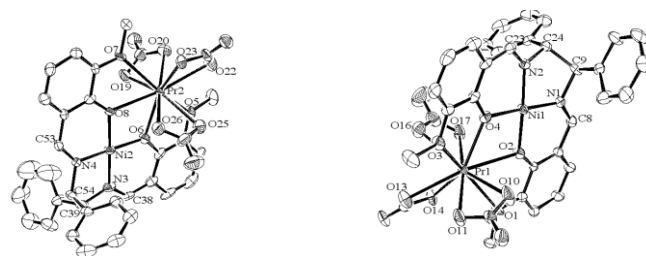


Figure 10. Molecular structures of **PrNi** showing selected atom labeling scheme. Hydrogen atoms are omitted clarity. Selected bond distance (Å) and bond or torsion angles (°): Ni1-N1 = 1.851(5), Ni1-N2 = 1.836(5), Ni1-O2 = 1.857(6), Ni1-O4 = 1.856(5), Pr1-O1 = 2.601(5), Pr1-O2 = 2.490(4), Pr1-O3 = 2.615(5), Pr1-O4 = 2.417(5), Ni2-N3 = 1.850(6), Ni2-N4 = 1.843(5), Ni2-O6 = 1.861(5), Ni2-O8 = 1.833(5), Pr2-O5 = 2.624(5), Pr2-O6 = 2.444(5), Pr2-O7 = 2.576(5), Pr2-O8 = 2.470(4), N1-Ni1-N2 = 86.5(2), O2-Ni1-N1 = 94.8(2), O2-Ni1-N2 = 176.7(2), O2-Ni1-O4 = 84.4(2), O4-Ni1-N1 = 177.6(2), O4-Ni1-N2 = 94.4(2), O1-Pr1-O2 = 60.33(17), O1-Pr1-O3 = 57.57(16), O1-Pr1-O4 = 121.34(16), O2-Pr1-O3 = 118.62(7), O2-Pr1-O4 = 61.11(17), O3-Pr1-O4 = 61.30(16), N3-Ni2-N4 = 86.9(2), O6-Ni2-N3 = 94.7(3), O6-Ni2-N4 = 74.0(2), O6-Ni2-O8 = 83.9(2), O8-Ni2-N3 = 175.5(2), O8-Ni2-N4 = 95.00(2), O5-Pr2-O6 = 62.03(18), O5-Pr2-O7 = 156.34(16), O5-Pr2-O8 = 120.45(18), O6-Pr2-O7 = 120.50(17), O6-Pr2-O8 = 60.32(17), O7-Pr2-O8 = 61.15(17).

Figure 11 depicts structure of **LuNi**. Ni(II) ion affords a 4-coordinated distorted square planar geometry without methanol ligands and Lu(III) ion affords a 10-coordinated environment with distorted square pyramidal from the plane made by two nitrate ligands. Phenyl groups connected to the asymmetric carbon atoms are located under a salen-plane with C40-C39-C54-C55 = 166.2(5) and C10-C9-C24-C25 = 155.5(6) °.

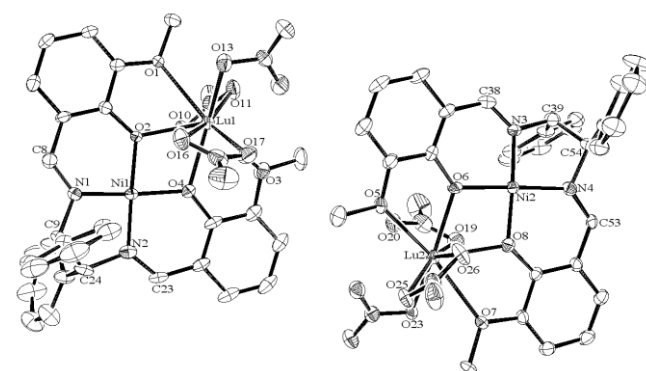


Figure 11. Molecular structures of **LuNi** showing selected atom labeling scheme. Hydrogen atoms are omitted clarity. Selected bond distance (Å) and bond or torsion angles (°): Ni1-N1 = 1.835(6), Ni1-N2 = 1.834(6), Ni1-O2 = 1.833(5), Ni1-O4 = 1.846(5), Lu1-O1 = 2.522(5), Lu1-O2 = 2.313(4), Lu1-O3 = 2.508(5), Lu1-O4 = 2.275(5), Ni2-N3 = 1.837(6), Ni2-N4 = 1.829(6), Ni2-O6 = 1.835(5), Ni2-O8 = 1.828(6), Lu2-O5 = 2.484(5), Lu2-O6 = 2.271(5), Lu2-O7 = 2.530(5), Lu2-O8 = 2.363(4), N1-Ni1-N2 = 86.9(3), O2-Ni1-N1 = 96.1(2), O2-Ni1-

$N2 = 175.0(2)$, $O2-Ni1-O4 = 81.5(2)$, $O4-Ni1-N1 = 172.8(2)$, $O4-Ni1-N2 = 96.1(2)$, $O1-Lu1-O2 = 60.10(18)$, $O1-Lu1-O3 = 150.47(16)$, $O1-Lu1-O4 = 124.11(17)$, $O2-Lu1-O3 = 125.41(19)$, $O2-Lu1-O4 = 63.10(18)$, $O3-Lu1-O4 = 64.96(19)$, $N3-Ni2-N4 = 86.9(2)$, $O6-Ni2-N3 = 94.6(2)$, $O6-Ni2-N4 = 178.2(2)$, $O6-Ni2-O8 = 82.9(2)$, $O8-Ni2-N3 = 176.8(2)$, $O8-Ni2-N4 = 95.6(2)$, $O5-Lu2-O6 = 64.83(17)$, $O5-Lu2-O7 = 151.07(16)$, $O5-Lu2-O8 = 122.70(19)$, $O6-Lu2-O7 = 125.10(17)$, $O6-Lu2-O8 = 63.09(19)$, $O7-Lu2-O8 = 62.33(18)$.

Figure 12 depicts structure of **LuCu** containing different two types of molecules in an asymmetric unit. Cu(II) ion affords a 4-coordinated compressed tetrahedral geometry, and Lu(III) ion affords 9- and 10-coordinated environments with distorted square pyramidal towards a coordinated methanol ligand or a bridging nitrate ligand.

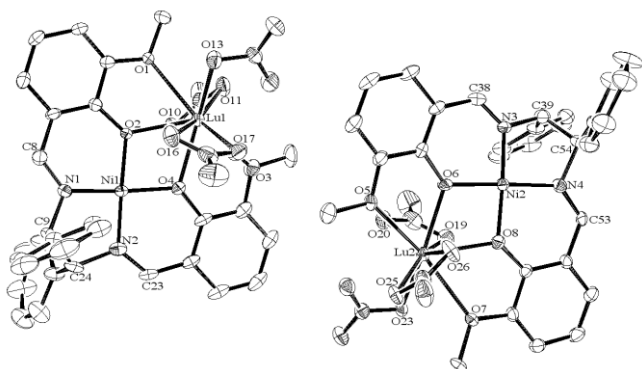


Figure 12. Molecular structures of **LuCu** showing selected atom labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distance (Å) and bond or torsion angles (°): Cu1-N1 = 1.835(6), Cu1-N2 = 1.834(6), Cu1-O2 = 1.833(5), Cu1-O4 = 1.846(5), Lu1-O1 = 2.522(5), Lu1-O2 = 2.313(4), Lu1-O3 = 2.508(5), Lu1-O4 = 2.275(5), Cu2-N3 = 1.837(6), Cu2-N4 = 1.829(6), Cu2-O6 = 1.835(5), Cu2-O8 = 1.828(6), Lu2-O5 = 2.484(5), Lu2-O6 = 2.271(5), Lu2-O7 = 2.530(5), Lu2-O8 = 2.363(4), N1-Cu1-N2 = 86.9(3), O2-Cu1-N1 = 96.1(2), O2-Cu1-N2 = 175.0(2), O2-Cu1-O4 = 81.5(2), O4-Cu1-N1 = 172.8(2), O4-Cu1-N2 = 96.1(2), O1-Lu1-O2 = 60.10(18), O1-Lu1-O3 = 150.47(16), O1-Lu1-O4 = 124.11(17), O2-Lu1-O3 = 125.41(19), O2-Lu1-O4 = 63.10(18), O3-Lu1-O4 = 64.96(19), N3-Cu2-N4 = 86.9(2), O6-Cu2-N3 = 94.6(2), O6-Cu2-N4 = 178.2(2), O6-Cu2-O8 = 82.9(2), O8-Cu2-N3 = 176.8(2), O8-Cu2-N4 = 95.6(2), O5-Lu2-O6 = 64.83(17), O5-Lu2-O7 = 151.07(16), O5-Lu2-O8 = 122.70(19), O6-Lu2-O7 = 125.10(17), O6-Lu2-O8 = 63.09(19), O7-Lu2-O8 = 62.33(18).

Figure 13 depicts structure of **LuZn**. Zn(II) ion affords a 5-coordinated square distorted pyramidal geometry lifted up towards axial methanol ligands and Lu(III) ion affords a 9-coordinated environment with distorted square pyramidal towards bridging nitrate ligands. Phenyl groups connected to asymmetric carbon atoms indicate slight distortion with C40-C39-C54-C55 = 56.0(8) and C25-C24-C9-C10 = 65.4(8)°.

Conclusion

In summary, we have prepared and structurally characterized seven 3d-4f binuclear complexes incorporating chiral salen-type Schiff base ligands. According to lanthanide contraction, the order of ion radii for the present 4f ions are Lu(III) ($4f^{14}$) < Pr(III) ($4f^2$) < Ce(III) ($4f^1$). For 4f ions, Ce-complexes and Pr-complexes adopted coordination number 10, which are

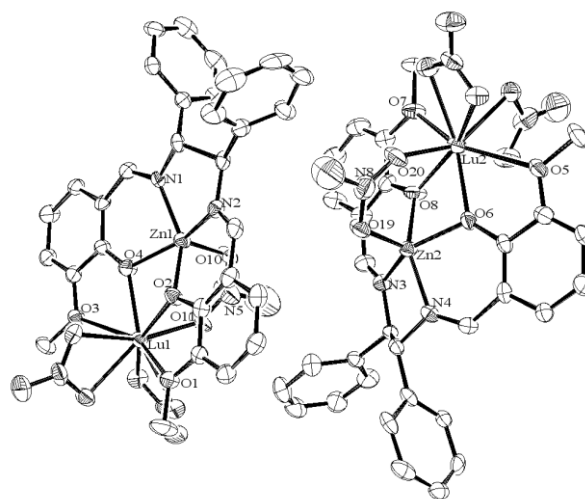


Figure 13. Molecular structures of **LuZn** showing selected atom labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distance (Å) and bond or torsion angles (°): Zn1-N1 = 2.004(6), Zn1-N2 = 2.021(6), Zn1-O2 = 1.999(5), Zn1-O4 = 2.014(5), Lu1-O1 = 2.562(5), Lu1-O2 = 2.282(5), Lu1-O3 = 2.603(5), Lu1-O4 = 2.229(6), Zn2-N3 = 2.041(6), Zn2-N4 = 2.016(6), Zn2-O6 = 2.019(5), Zn2-O8 = 2.011(5), Lu2-O5 = 2.627(6), Lu2-O6 = 2.232(5), Lu2-O7 = 2.568(5), Lu2-O8 = 2.238(5), N1-Zn1-N2 = 83.2(2), O2-Zn1-N1 = 143.7(2), O2-Zn1-N2 = 91.5(2), O2-Zn1-O4 = 77.4(2), O4-Zn1-N1 = 91.0(2), O4-Zn1-N2 = 152.6(2), O1-Lu1-O2 = 61.9(2), O1-Lu1-O3 = 151.5(2), O1-Lu1-O4 = 127.8(2), O2-Lu1-O3 = 127.7(2), O2-Lu1-O4 = 67.6(2), O3-Lu1-O4 = 62.7(2), N3-Zn2-N4 = 82.2(2), O6-Zn2-N3 = 141.7(2), O6-Zn2-N4 = 90.6(2), O6-Zn2-O8 = 77.4(2), O8-Zn2-N3 = 89.9(2), O8-Zn2-N4 = 149.3(2), O5-Lu2-O6 = 61.6(2), O5-Lu2-O7 = 149.9(2), O5-Lu2-O8 = 124.6(2), O6-Lu2-O7 = 130.1(2), O6-Lu2-O8 = 68.6(2), O7-Lu2-O8 = 62.0(2).

similar to analogous 3d-4f complexes previously reported.^{17-18,20-21} However, Lu-complexes are 10-coordinated for **LuNi**, 9- and 10-coordinated for **LuCu**, and 9-coordinated for **LuZn**. Moreover, bridging modes of nitrate ligands of **CeCu** and **LuCu** (and resulting dimeric structure) are different from other complexes. For 3d ions, axial coordination of methanol ligands and degree of distortion from planar basal plane exhibited variety among the complexes. Therefore, the present examples of appropriate combination of 3d-4f ions only by substituting three 3d ions and three 4f ions indicated drastic variety of crystal structures including crystalline solvents nevertheless of the identical chiral organic ligands.

Supplementary data

CCDC 864541 - 864545 contain the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

This work was supported by Research Foundation for Opto-Science and Technology.

References

- ¹Yang, X.-P., Jones, R. A., Wong, W.-K., Lynch, V., Oye, M., M., Holmes, A. L., *Chem. Commun.*, **2006**, 1836.
- ²Burrow, C. E., Burchell, T. J. Lin, P.-H. Habib, P., Wernsdorfer, W. Clerac, R., Murugesu, M., *Inorg. Chem.*, **2009**, *48*, 8051.
- ³Wong, W.-K. Yang, X., Jones, R. A., Rivers, J. H., Lynch, V., Lo, W.-K., Xiao, D., Oye, M. M., Holmes, A. L., *Inorg. Chem.*, **2006**, *45*, 4340.
- ⁴Pasatoiu, T. D., Madalan, A. M., Kumke, M. U., Tiseanu, C., Andruh, M., *Inorg. Chem.*, **2010**, *49*, 2310.
- ⁵Andruh, M., Costes, J.-P., Diaz, C., Gao, S., *Inorg. Chem.*, **2009**, *48*, 3342.
- ⁶Colacio, E., Ruiz, J., Mota, A. J., Palacios, M. A., Cremades, E., Ruiz, E., White, F. J., Brechin, E. K., *Inorg. Chem.*, **2012**, *51*, 5857.
- ⁷Yan, P.-F., Lin, P.-H. Habib, F. Aharen, T. Murugesu, M. Deng, Z.-P. Li, G.-M., Sun W.-B., *Inorg. Chem.*, **2011**, *50*, 7059.
- ⁸Colacio, E., Ruiz-Sanchez, J., White, F. J., Brechin, E. K., *Inorg. Chem.*, **2011**, *50*, 7268.
- ⁹Jana, A., Majumder, S., Carrella, L., Nayak, M., Weyhermueller, T., Dutta, S. Schollmeyer, D., Rentschler, E., Koner, R. Mohanta, S., *Inorg. Chem.*, **2010**, *49*, 9012.
- ¹⁰Feltham, H. L. C., Clerac, R., Ungur, L. Vieru, V. Chibotaru, L. F., Powell, A. K., Brooker, S., *Inorg. Chem.*, **2012**, *51*, 10603.
- ¹¹Margeat, O., Lacroix, P. G., Costes, J. P., Donnadieu, B., Lepetit, C., *Inorg. Chem.*, **2004**, *43*, 4743.
- ¹²Gomez, V., Vendier, L., Corbella, M., Costes, J.-P., *Inorg. Chem.*, **2012**, *51*, 6396.
- ¹³Figuerola, A., Diaz, C., Ribas, J., Tangoulis, V., Granell, J., Lloret, F., Mahia, J., Maestro, M., *Inorg. Chem.*, **2003**, *42*, 641.
- ¹⁴Li, G., Akitsu, T., Sato, O., Einaga, Y., *J. Am. Chem. Soc.*, **2003**, *125*, 12396.
- ¹⁵Svendsen, H., Overgaard, J., Chevallier, M., Collet, E., Iversen, B.B., *Angew. Chem. Int. Ed.*, **2009**, *48*, 2780.
- ¹⁶Akitsu, T., *Asian Chem. Lett.*, **2010**, *14*, 53 and references therein.
- ¹⁷Akitsu, T., Hirarsuka, T., Shibata, H., *Magnets: Types, Uses and Safety, Nova Science Publishers*, **2012** and references therein.
- ¹⁸Hirarsuka, T., Shibata, T. Akitsu, H., *Crystallography: Research, Technology and Applications, Nova Science Publishers*, **2012** and references therein.
- ¹⁹Sheldrick, G. M., *Acta Cryst.*, **2008**, *A64*, 112.
- ²⁰Bi, W.-Y., Lu, X.-Q., Chai, W.-L., Song, J.-R., Wong, W.-Y., Wong, W.-K., Jones, R. A., *J. Mol. Struct.*, **2008**, *891*, 450.
- ²¹Bi, W.-Y., Lu, X.-Q., Chai, W.-L., Jin, W.-J., Song, J.-R., Wong, W.-K., *Inorg. Chem. Commun.*, **2008**, *11*, 1316.

Received: 23.11.2012.

Accepted: 04.11.2012.