ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 6, pp. 396–400. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © V.F. Shul'gin, Z.Z. Bekirova, O.V. Konnik, S.B. Meshkova, A.V. Kiriyak, G.G. Aleksandrov, I.L. Eremenko, 2014, published in Koordinatsionnaya Khimiya, 2014, Vol. 40, No. 6, pp. 374–378.

To the 80th anniversary of the Kurnakov Institute
of General and Inorganic Chemistry, Russian Academy of Sciences

Coordination Compounds of Neodymium(III) with Acyldihydrazones of Saturated Dicarboxylic Acids and 3-Methyl-1-Phenyl-4-Formylpyrazol-5-one

V. F. Shul'gin[a, *], Z. Z. Bekirova[a], O. V. Konnik[a], S. B. Meshkova[b], A. V. Kiriyak[b],
G. G. Aleksandrov[c], and I. L. Eremenko[c]

[a] *Taurida National V.I. Vernadsky University, pr. Vernadskogo 4, Simferopol, Ukraine*
[b] *Bogatskii Physicochemical Institute, National Academy of Sciences of Ukraine,*
Chernomorskaya doroga 86, Odessa, Ukraine
[c] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
Leninskii pr. 31, Moscow, 119991 Russia
**e-mail: vshul@crimea.edu*

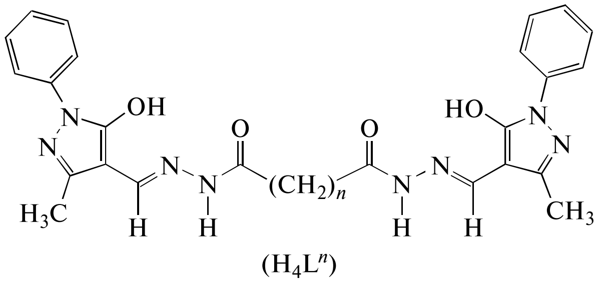
Received October 16, 2013

Abstract—Coordination compounds of neodymium(III) with acylhydrazones of saturated dicarboxylic acids and 3-methyl-1-phenyl-4-formylpyrazol-5-one are synthesized and studied. The structure of complex $[Nd_2(H_2L^2)_3] \cdot Me_2SO \cdot CH_3OH \cdot 6H_2O$ is determined from the X-ray diffraction data for the isostructural lanthanum complex. The complex is binuclear and contains nine-vertex coordination polyhedra bound by three hydrocarbon spacers. Solid samples of the studied neodymium complexes exhibit luminescence in the near-infrared spectral range (λ = 874, 904, and 1059 nm) characteristic of this ion.

DOI: 10.1134/S1070328414060074

INTRODUCTION

Interest in coordination compounds of lanthanides with 4-acylpyrazolones and their derivatives is primarily due to the search for new highly efficient luminophores and, hence, this class of complexes was studied in detail [1–4]. At the same time, coordinating possibilities of some 4-acylpyrazole derivatives, for example, acylhydrazones, are presently studied insufficiently. This work is devoted to the study of specific features of the molecular structure and optical properties of the binuclear neodymium(III) complexes with acyldihydrazones of saturated dicarboxylic acids (H_4L^n), where n = 1–4 and 3-methyl-1-phenyl-4-formylpyrazol-5-one.



(H_4L^n)

The coordination compounds of lanthanides with 3-methyl-1-phenyl-4-formylpyrazol-5-one have been described previously [5, 6].

EXPERIMENTAL

Synthesis. Dihydrazide of the corresponding dicarboxylic acid (0.0015 mol) was added to a solution of 3-methyl-1-phenyl-4-formylpyrazol-5-one (0.0030 mol) [7] in ethanol (20 mL). The mixture was magnetically stirred with slight heating for 2 h. Pyridine (10 mL) and neodymium(III) nitrate (0.001 mol) in an ethanol solution (15 mL) were added to the formed suspension. The formed solution was magnetically stirred for 30 min and left overnight. The precipitate formed was separated by filtration, washed with ethanol, and dried in air. A light lilac finely crystalline substance was obtained in a yield of 70–85%. According to the elemental and thermal analyses data, the composition of the complexes corresponds to the formula $[Nd_2(H_2L^n)_3] \cdot Solv$ (n = 1–4).

For $[Nd_2(H_2L^1)_3] \cdot 23H_2O$ ($C_{75}H_{112}N_{24}O_{35}Nd_2$; **I**)

anal. calcd., %:	C, 40.98;	H, 5.10.
Found, %:	C, 40.35;	H, 4.23.

IR (ν_{max}, cm^{-1}): 1642, 1622, 1530, 1502.

For $[Nd_2(H_2L^2)_3] \cdot C_2H_5OH \cdot 20H_2O$ ($C_{80}H_{118}N_{24}O_{33}Nd_2$; **II**)

anal. calcd., %:	C, 43.05;	H, 5.30.
Found, %:	C, 43.04;	H, 4.12.

IR (ν_{max}, cm^{-1}): 1628, 1620, 1534, 1500.

For $[Nd_2(H_2L^3)_3] \cdot C_2H_5OH \cdot 8H_2O$ ($C_{83}H_{100}N_{24}O_{21}Nd_2$; **III**)

anal. calcd., %:	C, 48.44;	H, 4.86
Found, %:	C, 48.72;	H, 4.71.

IR (ν_{max}, cm^{-1}): 1642, 1622, 1538, 1500.

For $[Nd_2(H_2L^4)_3] \cdot 2C_2H_5OH \cdot 8H_2O$ ($C_{88}H_{112}N_{24}O_{22}Nd_2$; **IV**)

anal. calcd., %:	C, 49.25;	H, 5.22.
Found, %:	C, 49.05;	H, 4.65.

IR (ν_{max}, cm^{-1}): 1632, 1622, 1538, 1502 ν(CO).

Thermogravimetric curves were obtained on a Q derivatograph (Paulik–Paulik–Erdey system) in a static air atmosphere (heating rate 10 K/min, uncapped ceramic crucible as a sample holder, calcined alumina as a standard). The IR spectra of the samples pressed with KBr were studied in the range from 4000 to 400 cm^{-1} on a PerkinElmer BX FT-IR spectrometer. Luminescence spectra were recorded on an SDL-1 diffraction spectrometer (LOMO) with a DRSh-250 mercury lamp picking out the radiation of the most intense line (λ = 365 nm) by an UFS-2 light filter.

Single crystals of $[Nd_2(H_2L^2)_3] \cdot Me_2SO \cdot CH_3OH \cdot 6H_2O$ (**V**) were grown by the recrystallization of complex **II** from a dimethyl sulfoxide–methanol (1 : 1 vol/vol) mixture. The space group and unit cell parameters ($P4_32_12$, a = 14.35 c = 56.06 Å, V = 11540 Å^3) were determined by X-ray diffraction analysis. Since the low quality of single crystals did not allow one to solve and refine the structure with a necessary accuracy, this problem was solved by the study of the complex with the composition $[La_2(H_2L^2)_3] \cdot Me_2SO \cdot CH_3OH \cdot 6H_2O$ (**VI**) isostructural to complex **V**.

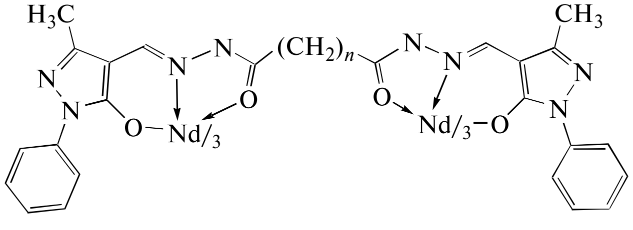
The X-ray diffraction analysis of complex **VI** was carried out on a Bruker Smart APEX II diffractometer equipped with a CCD detector and a monochromatic radiation source (MoK_α, λ = 0.71073 Å, graphite monochromator) using the standard procedure [8]. The structure was solved by a direct method and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were specified geometrically and refined in the riding model. Calculations were performed using the SHELXL97 program [9]. Experimental details are presented in Table 1. The full set of X-ray diffraction data was deposited with the Cambridge Crystallographic Data Centre (no. 881792; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystallographic data and determination details for the structure of complex $[La_2(H_2L)_3] \cdot Me_2SO \cdot CH_3OH \cdot 6H_2O$ (**VI**)

Parameter	Value
Empirical formula	$C_{82}H_{96}N_{24}O_{21}SLa_2$
Crystal size, mm	0.33 × 0.23 × 0.12
M	2063.71
Crystal system	Tetragonal
Space group	$P4_32_12$
a, Å	14.0258(15)
c, Å	55.541(6)
Z	4
V, Å^3	10926(2)
Temperature, K	296
μ, mm^{-1}	0.86
ρ_{calcd}, g/cm^3	1.255
θ range, deg	2.2–24.6
Index variation range	$-18 \le h \le 18$, $-18 \le k \le 17$, $-72 \le l \le 71$
Measured reflections	108508
Number of independent reflections	12518
R	0.077
wR	0.249
GOOF	1.001
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.05/–3.15

RESULTS AND DISCUSSION

The results of the studies indicate that the reactions of neodymium(III) nitrate with diacylhydrazones of saturated dicarboxylic acids and 3-methyl-1-phenyl-4-formylpyrazol-5-one afford binuclear complexes in which the coordination polyhedra are bound by three hydrocarbon bridges.



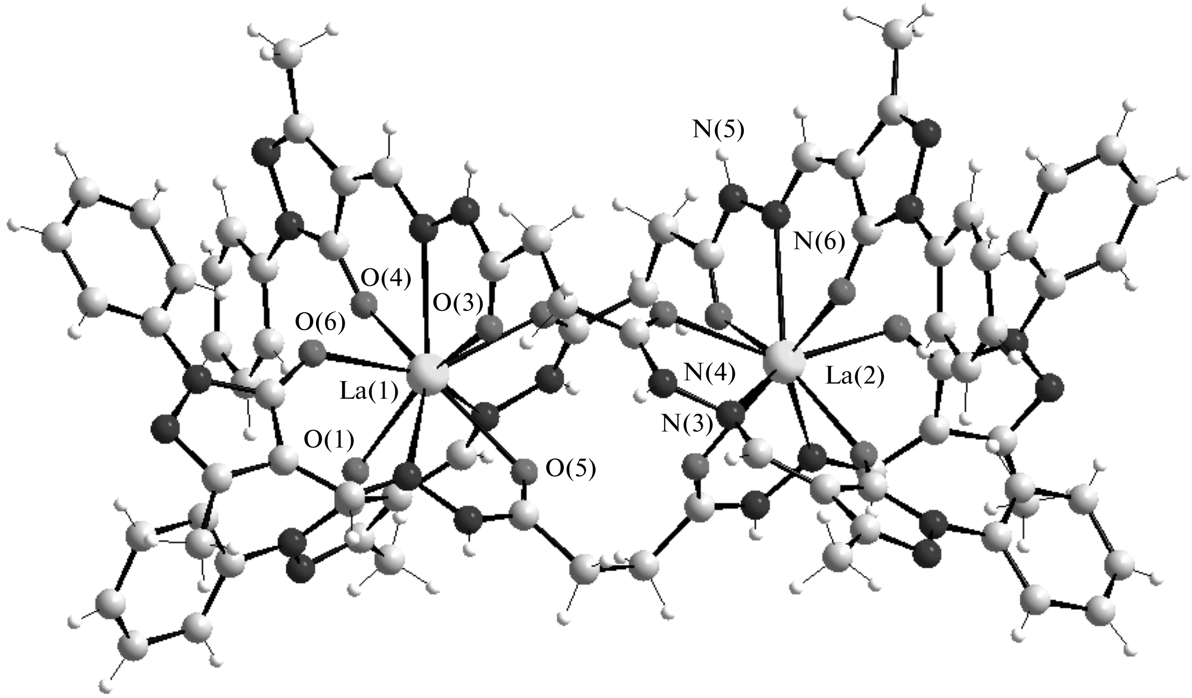


Fig. 1. General view and atomic numbering of the $[La_2(H_2L^2)_3]$ complex. Bond lengths and bond angles in the coordination polyhedron: La(1)–O(1) 2.424(6), La(1)–O(6) 2.447(6), La(1)–O(4) 2.447(6), La(1)–O(2) 2.528(6), La(1)–O(5) 2.549(6), La(1)–O(3) 2.567(6), La(1)–N(11) 2.730(7), La(1)–N(6) 2.746(8), and La(1)–N(3) 2.755(8) Å; O(1)La(1)O(6) 80.5(3)°, O(1)La(1)O(4) 80.3(3)°, O(6)La(1)O(4) 80.7(3)°, O(1)La(1)O(2) 130.0(2)°, O(6)La(1)O(2) 144.6(2)°, O(4)La(1)O(2) 87.0(2)°, O(1)La(1)O(5) 85.7(3)°, O(6)La(1)O(5) 130.4(2)°, O(4)La(1)O(5) 143.2(2)°, O(2)La(1)O(5) 76.3(2)°, O(1)La(1)O(3) 145.3(2)°, and O(6)La(1)O(3) 86.4(3)°.

The formation of coordination compounds **I–IV** result in changes in the IR spectra: the "amide I" band, which is detected at 1668 cm^{-1} for free ligands, is shifted to 1628–1642 cm^{-1}. The stretching vibration band of the azomethine group is shifted from 1612 to 1620–1622 cm^{-1}. The band corresponding to stretching vibrations of the C–O bond of the enol group in free ligands is detected at 1594 cm^{-1}. Upon coordination, this band is shifted to 1530–1538 cm^{-1}. The bands caused by the bending NNH vibrations of free ligands appear at 1494–1500 cm^{-1} and remain nearly unchanged upon complex formation, indicating the retention of the amide form of the hydrazone fragment.

According to the thermogravimetric data, complexes **I–IV** are desolvated in a fairly wide temperature range accompanied by a pronounced endotherm with a minimum in the DTA curve at 100–150°C. A poorly pronounced "plateau" corresponding to the stability region of the desolvated state is observed at 200–300°C in the TGA curve. The temperature increase to 300–450°C leads to a slow mass loss caused by the thermooxidative destruction of the binucleating ligand followed by burning out of the organic residue. The process is accompanied by the appearance of a broad exotherm with a maximum at 380–400°C in the DTA curve and stops at 500–600°C.

To establish the structures of the studied compounds, we carried out an X-ray diffraction analysis of lanthanum complex **VI** isostructural to similar neodymium complex **V** grown by the slow diffusion of methanol vapor into a saturated solution of compound **II** in DMSO.

Complex **VI** is dimeric. The La^{3+} cations are arranged at a distance of 6.895 Å from each other and are linked by the 2-fold symmetry axis (Fig. 1). Solvent molecules (dimethyl sulfoxide, methanol, water) occupy the out-of-sphere positions and are bound to each other and to the nitrogen atoms of the pyrazole cycles by a complicated lattice of hydrogen bonds, and the DMSO molecule is disordered.

The coordination polyhedron of the lanthanum atom is formed by three equivalent groups of the nitrogen and oxygen atoms of the deprotonated hydrazone group linked by three ethylene bridges. Taking into account that a similar structure has been described previously for the cerium complex with malonic acid bis(salicylidenehydrazone) [10], it can be assumed that this molecular architecture is typical of lanthanide complexes with extended binucleating ligands.

The coordination polyhedron of the La^{3+} cation can be described as a slightly distorted three-capped trigonal prism. The chelate cycles are nonplanar. The

Table 2. Luminescence characteristics of the Nd(III) complexes*

Compound	Transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$				Transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$	
	λ_{max}, nm	I_{lum}	λ_{max}, nm	I_{lum}	λ_{max}, nm	I_{lum}
I	874	53	902	50	1058	31
II	874	52	904	47	1059	31
III	872	176	903	106	1056	63
IV	872	111	903	86	1057	55

* The values of I_{lum} (rel. units) are reduced to equivalent experimental conditions.

lanthanum atom deviates from the planes of the five-membered metallocycles by 0.026–0.236 Å. The deviations of atoms from the plane of the chelating group of the six-membered metallocycle attain 0.341–0.567 Å. The bond lengths of the lanthanum cation with the phenol oxygen atoms in complex **VI** (2.424–2.447 Å) fall in the range of values characteristic of lanthanum phenoxides (2.23–2.46 Å) [11]. The

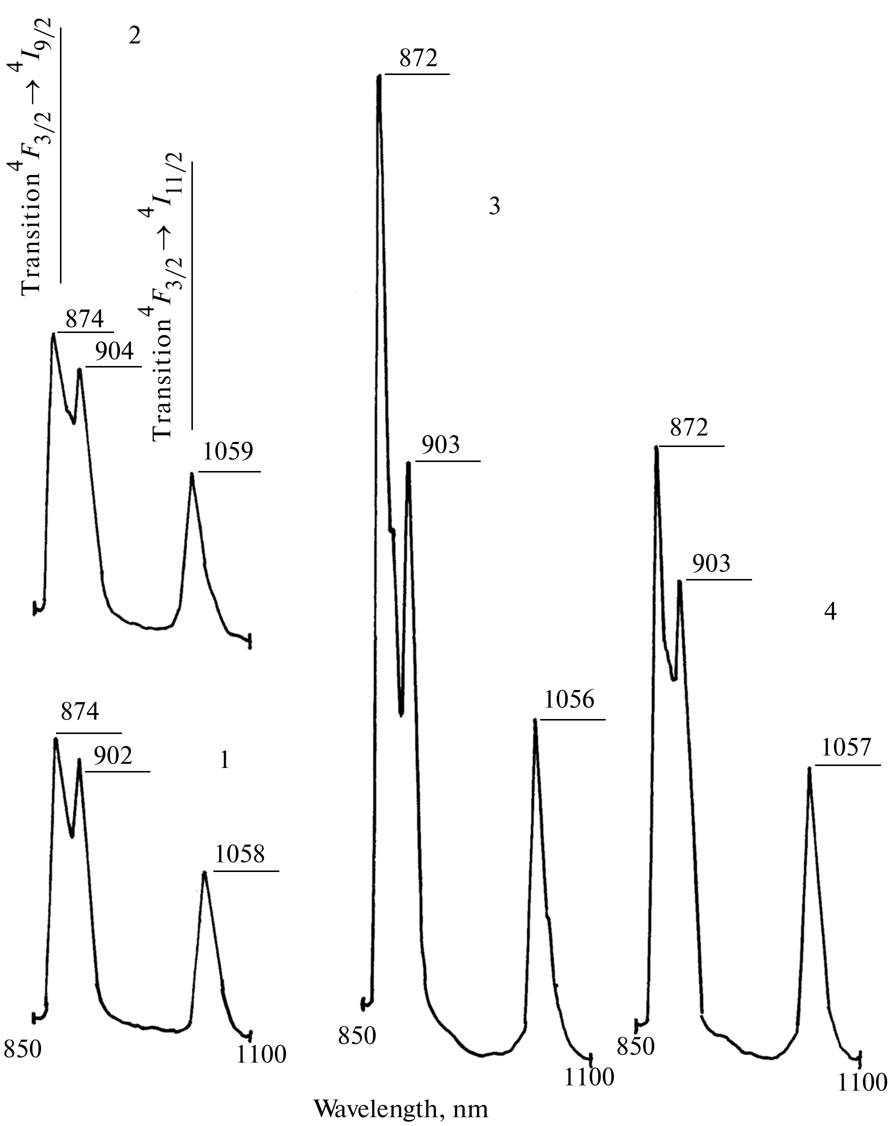


Fig. 2. Luminescence spectra of the neodymium(III) complexes at different lengths of the hydrocarbon spacer: (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV** for $n = 1, 2, 3$, and 4, respectively.

lengths of lanthanum with the amide oxygen atoms are longer (2.528–2.567 Å). The nitrogen atoms are more remote from the lanthanum cation (La–N 2.730–2.755 Å).

The C–O (amide) bonds in complex **VI** (1.116–1.239 Å) are somewhat shortened compared to the phenol C–O bonds (1.231–1.264 Å). The latter differ strongly from the values of standard ordinary carbon–oxygen bonds due to delocalization in the hydrazone group. The bond lengths and bond angles in the rest part of the organic ligands are close to standard values [12].

The luminescence spectra of the Nd(III) complexes (Table 2, Fig. 2) exhibit a sharp splitting of the luminescence band corresponding to the transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$ with two maxima at 872 and 903 nm, indicating a low symmetry of the coordination polyhedron. As the number of CH_2 groups increases in the spacer connecting the complexing moieties of the ligand, the luminescence intensity of Nd(III) at first remains unchanged (compounds **I** and **II**) and then passes through a maximum (compound **III**). The further elongation of the spacer in compound **IV** decreases the luminescence intensity of Nd(III), most likely, due to a decrease in the rigidity of the polymethylene spacer.

Thus, diacylhydrazones obtained by the condensation of dihydrazides of saturated dicarboxylic acids and 3-methyl-1-phenyl-4-formylpyrazol-5-one are efficient binucleating ligands suitable for the formation of coordination compounds with the neodymium(III) ion and for the observation of its narrow-band IR luminescence caused by the intramolecular energy transfer to the central ion from the ligand in the excited state.

REFERENCES

1. Katkova, M.A., Vitukhnovskii, A.G., and Bochkareva, M.N., *Usp. Khim.,* 2005, vol. 74, no. 12, p. 1193.
2. Binnemans, K., *Chem. Rev.*, 2009, vol. 109, p. 4283.
3. Marchetti, F., Pettinari, C., and Pettinari, R., *Coord. Chem. Rev.*, 2005, vol. 249, p. 2909.
4. Casas, J.S., Garcia-Tasende, M.S., Sanchez, A., et al., *Coord. Chem. Rev.,* 2007, vol. 251, p. 1561.
5. Shul'gin, V.F., Abkhairova, S.V., Konnik, O.V., et al., *Russ. J. Inorg. Chem.*, 2012, vol. 57, no. 3, p. 420.
6. Meshkova, S.B., Topylova, Z.M., Shul'gin, V.F., et al., *1st Intern. Conf. on Luminescence of Lanthanides*, Odessa (Ukraine), 2010, p. 92.
7. Kvitko, I.Ya. and Porai-Koshits, B.A., *Zh. Org. Khim.*, 1964, vol. 34, no. 9, p. 3005.
8. *SMART (control) and SAINT (integration) Sofware. Version 5.0*, Madison (WI, USA): Bruker AXS Inc., 1997.
9. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
10. Zhu, X., He, C., Dong, D., et al., *Dalton Trans.*, 2010, vol. 39, no. 42, p. 10051.
11. Boyle, T. and Ottley, A.M., *Chem. Rev.*, 2008, vol. 108, no. 6, p. 1896.
12. Allen, F.H., Kennard, O., Watson, D.G., et al., *J. Chem. Soc., Perkin Trans.*, 1987, no. 12.

Translated by E. Yablonskaya