

Proceedings of the 2nd Winter Workshop S&SRES'96, Polanica Zdrój 1996

OPTICAL PROPERTIES AND STRUCTURE OF $\text{Ln}(\text{NCS})(\text{Hmpa})_4-(\text{SCN})_2\text{-HgCl}(\text{SCN})$

E. GALDECKA

Institute for Low Temperature and Structure Research, Polish Academy of Sciences
Okólna 2, 50-950 Wrocław, Poland

Z. GALDECKI

Institute of General and Ecological Chemistry, Technical University of Łódź
Żwirki 36, 90-924 Łódź, Poland

V. AMIRKHANOV

Department of Chemistry, Kiev State University
Vladimirskaya 64, 252033 Kiev, Ukraine

K. KERN AND J. LEGENDZIEWICZ*

Faculty of Chemistry, University of Wrocław
F. Joliot-Curie 14, 50-383 Wrocław, Poland

Praseodymium, neodymium and europium complexes of the formula $\text{Ln}(\text{NCS})(\text{Hmpa})_4-(\text{SCN})_2\text{-HgCl}(\text{SCN})$ were synthesised from non-aqueous solutions. The structure of neodymium complexes was determined by X-ray diffraction. The crystals of the title compounds crystallise in the space group Cc , where lanthanide ions are coordinated to seven ligand groups: four of Hmpa molecules and three SCN^- ions. The compounds were characterised by IR, luminescence, excitation and absorption spectra at 6, 77, and 298 K. Probabilities of electronic transitions for Pr^{3+} ion were examined at 6 K and at room temperatures. Vibronic components were observed and analysed on the basis of IR and Raman data. Asymmetric arrangement of Ln ions was found from X-ray analysis and its influence on optical properties of active centre was discussed.

PACS numbers: 78.20.Wc, 78.55.Hx, 78.20.Dj, 78.66.-w, 61.66.Fn

1. Introduction

In recent period a great interest has been focused on binuclear lanthanide complexes, composed of two different lanthanide ions, a lanthanide and a d -electron metal or a diamagnetic transition metal ion.

* Author to whom correspondence should be addressed.

The metal ions in mixed binuclear complexes can help in understanding different types of interactions and their effect on radiative and nonradiative transitions. A few years ago we published spectroscopic results for lanthanide dimer systems with centro- and noncentrosymmetric dimeric units [1–4]. Now we present spectroscopy and structure of a different kind of dimer: single crystals of Ln–Hg type. The main goal of this paper is to study the influence of heavy metal ion on non-radiative quenching of lanthanide emission, as well as the influence of asymmetric arrangement around lanthanide ions (on one side given by ligands with different polarizabilities, on the other by neighbour Hg²⁺ ion) on intensities of *f–f* transitions, especially the hypersensitive ones. We try also to examine the vibronic coupling in the systems under investigation.

Binuclear architecture La(NCS)(Hmpa)₅–(NCS)–HgCl(SCN)₂ system was concluded from X-ray analysis [5]. Other lanthanide ions form complexes of somewhat different composition and with different structures. In now presented studies, an attempt was made to characterise optical properties and structure of Pr, Nd, and Eu–Hg complexes.

2. Experimental

Single crystals of formulae Ln(NCS)₄(Hmpa)₄–HgCl (Ln = Pr, Nd, Eu) were synthesised in acetone solution. A Siemens P3 diffractometer was used for data collection.

Selected interatomic distances and angles are presented in Table I. A full X-ray analysis will be the subject of the separate paper [6].

TABLE I
Selected interatomic distances (Å) and angles (°) in
Nd(SCN)₄(Hmpa)₄HgCl.

Bond lengths [Å]		Bond angles [°]	
Nd–O(1)	2.317(14)	Nd–O(1)–P(1)	166.3(14)
Nd–O(2)	2.395(15)	Nd–O(2)–P(2)	165.9(13)
Nd–O(4)	2.356(15)	Nd–O(4)–P(4)	166.7(11)
Nd–O(5)	2.331(20)	Nd–O(5)–P(5)	161.5(10)
Nd–N(1)	2.626(31)	Nd–N(1)–C(1)	158.7(21)
Nd–N(3)	2.623(26)	Nd–N(3)–C(3)	156.0(21)
Nd–N(4)	2.441(23)	Nd–N(4)–C(4)	177.7(25)
Hg–Cl	2.506(12)		
Hg–S(1)	2.628(8)		
Hg–S(2)	2.618(19)		
Hg–S(3)	2.396(11)		

The absorption spectra in 5–293 K temperature range were measured by a Cary-Varian 5 spectrophotometer equipped with an Oxford helium flow cryostat.

The excitation and emission spectra were recorded at 77 and 293 K using an Aminco SPR 500 spectrofluorometer. The IR spectra were done in 50–2300 cm^{-1} range using a Bruker FS 88 FTIR spectrometer. Raman spectra were measured by a DFS 24 double monochromator ($f = 0.82$ m) equipped with photon counting system. The excitation source was argon ion laser ($\lambda = 514.3$ and 488 nm).

3. Results and discussion

Figure 1 shows a view of the structure of a binuclear crystal of title compound. The lanthanide ion is bridged by two SCN^- ions with the mercury atom, which is placed in a four-coordinated environment given additionally by Cl^- anion and monodentate SCN^- ion linked by a sulphur atom with the mercury one. The lanthanide ion is sevenfold coordinated by oxygen atoms of four Hmpa molecules, by the monodentate isothiocyanate group bonded to it by its N atom, and by two bridging SCN^- anions. These latter groups link the Ln^{3+} ion to mercury by N and S atoms, as shown in Fig. 1. In such the manner an asymmetric surrounding of lanthanide ion was created, and its asymmetry becomes deeper because of the presence of mercury ion bridged to the Ln one. In sites opposite to monodentate SCN^- groups, there are located the Hmpa molecules.

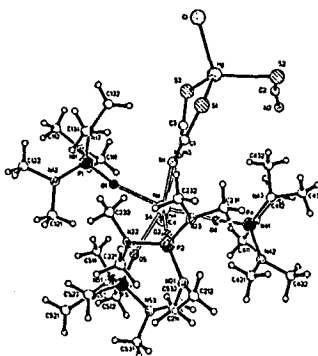


Fig. 1. General view of the molecule of $\text{Nd}(\text{NCS})(\text{Hmpa})_4-(\text{NCS})_2\text{-HgCl}(\text{SCN})$.

Our previous IR data indicate some differences in creation of structures of lanthanum and praseodymium complexes [7].

The aim of our spectroscopic studies was to explain, how far the asymmetric arrangement of lanthanide ions with two types of molecules with different polarizabilities, of rather rare for lanthanides coordination number ($\text{C.N.} = 7$) affects the optical properties of the compounds under consideration. Another question is, to what extent the ν_{CN} vibration mode (of relatively high energy 2055–2130 cm^{-1}) influences the emission properties of lanthanide ions.

Absorption spectra of praseodymium single crystals (at 293 and 6–10 K) were measured (Fig. 2) and calculated intensities of $f-f$ transitions are collected in Table II. Unexpectedly low intensities were observed in the regions of both ${}^3\text{H}_4 \rightarrow {}^3\text{P}_J$ and ${}^3\text{F}_J$ transitions. Lowering of temperature down to ≈ 10 K leads to

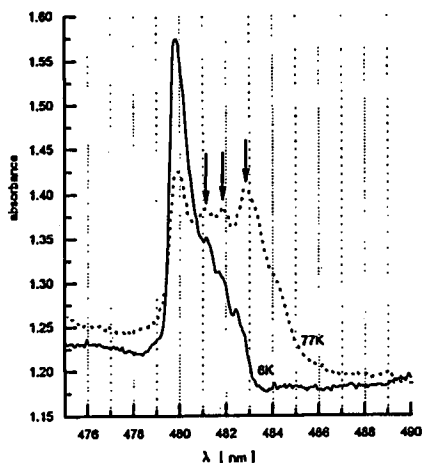


Fig. 2. The absorption spectra of $\text{Pr}(\text{NCS})(\text{Hmpa})_4-(\text{NCS})_2\text{-HgCl}(\text{SCN})$ in the range of ${}^3H_4 \rightarrow {}^3P_0$ transition at 77 and 6 K.

TABLE II
The oscillator strength values of $\text{Pr}(\text{SCN})_4(\text{Hmpa})_4\text{HgCl}$ single crystals.

Transitions	$P \times 10^8$		
	$C_{\text{Pr}} = 1.1595 \text{ [mol/dm}^3\text{]}$		5 K
	293 K		
	x	y	
${}^3H_4 \rightarrow {}^3P_2$	1397.92	1313.58	1447.64
${}^3H_4 \rightarrow {}^3P_1, {}^1I_6$	560.69	550.61	392.45
${}^3H_4 \rightarrow {}^3P_0$	281.62	281.39	105.50
${}^3H_4 \rightarrow {}^1D_2$	410.04		291.51
${}^3H_4 \rightarrow {}^1G_4$	44.46		
${}^3H_4 \rightarrow {}^3F_4$	130.09		
${}^3H_4 \rightarrow {}^3F_3$	564.06		

a decrease in oscillator strength values of the bands corresponding to transitions from 3H_4 multiplet to ${}^3P_{0,1}$ and 1D_2 levels. Intensity of ${}^3H_4 \rightarrow {}^3P_2$ transition increases rather a little. The intensities of these transitions are low compared to other available praseodymium results [1, 2, 4, 8].

Calculations were performed for two orientations of crystals, in fact, they give little opportunity to suppose a drastic increase in intensities at the third orientation of the crystal.

The temperature dependence of absorption spectra down to ≈ 10 K indicates a complex structure of 3P_0 bands, caused by population of the low-lying Stark

components of the ground state multiplet. In this way it was possible to distinguish partially the splitting of 3H_4 level (Fig. 2).

The most interesting and important seems to be examination of luminescence and excitation spectra of europium binuclear systems. Relatively strong emission was detected at room temperature with the complex structure of bands (Figs. 3 and 4). Group theory considerations of splitting of the 7F_J levels in the spectra of europium binuclear crystals allowed us to determine C_{2v} or C_s point symmetry of M^{3+} in the sevenfold coordination polyhedra. It confirms also a distortion of the ideal polyhedron with C.N. = 7 in the system under investigation. Furthermore, additional components observed in the transitions which obey the selection rule $\Delta J = 0, 2$, both in emission and excitation spectra at 77 K (Figs. 3 and 4), show a relatively strong vibronic coupling with external and internal ligand modes, especially with ν_{PO} and ν_{CN} at ≈ 1100 and ≈ 2100 cm^{-1} .

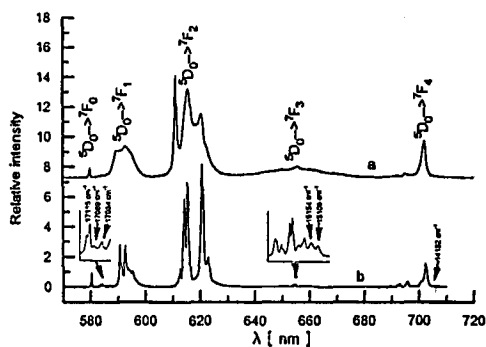


Fig. 3. The luminescence spectra of $\text{Eu}(\text{NCS})(\text{Hmpa})_4-(\text{NCS})_2-\text{HgCl}(\text{SCN})$ at 293 K (a) and 77 K (b).

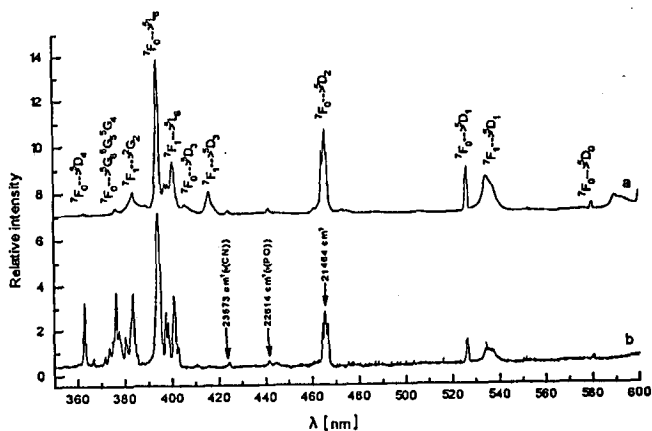


Fig. 4. The excitation spectra of $\text{Eu}(\text{NCS})(\text{Hmpa})_4-(\text{NCS})_2-\text{HgCl}(\text{SCN})$ at 293 K (a) and 77 K (b).

TABLE III

The electronic and vibronic components in emission and excitation spectra of $\text{Eu}(\text{SCN})_4(\text{Hmpa})_4\text{HgCl}$ at 77 K.

Transition.	Energy [cm^{-1}]	ΔE (from 0-phonon line) [cm^{-1}]		
		17232 (1)	16284 (2)	16108 (3)
${}^5D_0 \rightarrow {}^7F_0$ (1)	17232			
	17135	97		
	17115	117		
	17089	143		
	17034	198		
	16835	397		
	16762	440		
${}^5D_0 \rightarrow {}^5F_2$ (2) (3)	16284			
	16108			
	15154		1130 ($\nu(\text{PO})$)	
		2123 ($\nu(\text{CN})$)		
	15109			
	14977			1131 ($\nu(\text{PO})$)
	14152		2132 ($\nu(\text{CN})$)	
${}^7F_0 \rightarrow {}^5D_2$	21464			
	22614	1150 ($\nu(\text{PO})$)		
	23573	2109 ($\nu(\text{CN})$)		

Assignments of vibronic components in the electronic transitions was made on the basis of IR and Raman data (Fig. 5a, b). In Table III the vibronic components found both in excitation and emission spectra of europium single crystal are included. It is not the intention of the present paper to perform fully the vibronic analysis, thus the attribution was made only for the most effective ligand modes in the vibronic coupling.

IR spectra of all the investigated complexes have an absorption band in the region of 1120–1135 cm^{-1} , which belongs to stretching vibration of the P–O bond, coordinated by oxygen of the Hmpa ligand. One can note the strong P–O frequency shift in complexes with lanthanide, in comparison to ν_{PO} frequency of the PO group in free ligand ($\Delta\nu_{\text{PO}}$ amounts to 75–85 cm^{-1}). In the region of CN vibrations (2055–2130 cm^{-1}) we observed two absorption bands. The low-frequency one belongs to the monodentate SCN^- group, and the high-frequency — to the bridging thiocyanato group.

An interesting effect was reached, showing a strong coupling with ν_{CN} modes of relatively high energy (2100 cm^{-1}). One would await that this mode could be active in quenching of europium fluorescence. However, this nonradiative process is not effective enough, since the luminescence was detected at room temperature (Fig. 3).

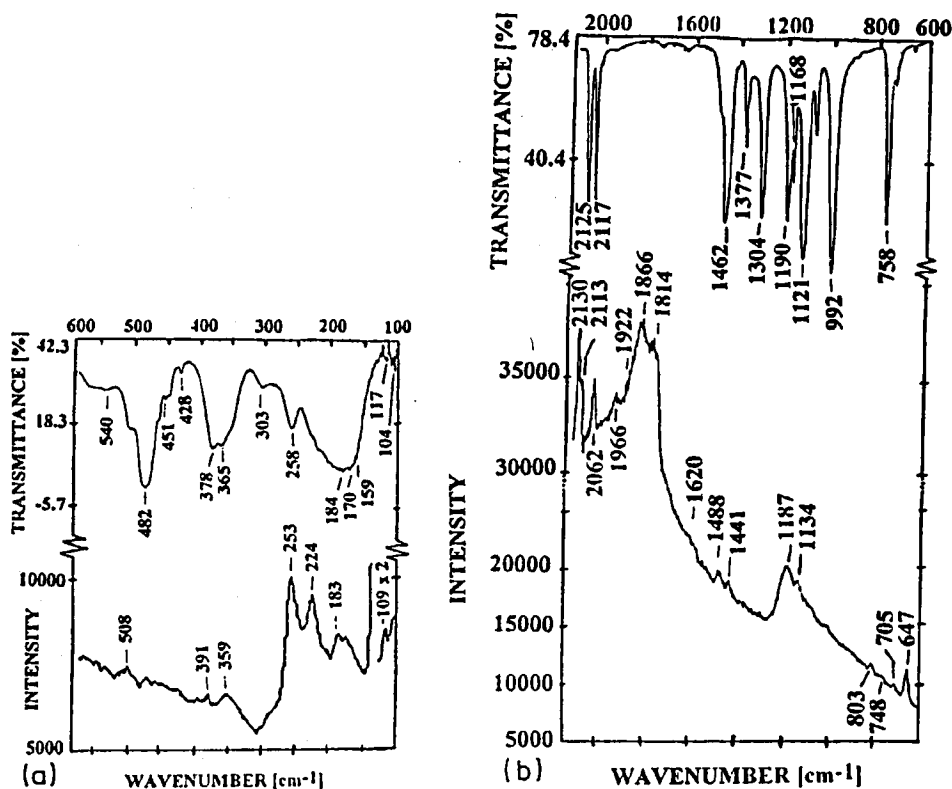


Fig. 5. IR (a) and Raman (b) spectra of Pr(NCS)(Hmpa)₄(NCS)₂ · HgCl(SCN) crystal.

Confrontation of the excitation spectra in the range of ${}^7F_0 \rightarrow {}^5D_J$ bands with the luminescence spectra in the region of ${}^5D_0 \rightarrow {}^7F_J$ levels at 77 K (Figs. 3 and 4) indicate significant differences in the splitting of respective transitions of the same ΔJ . This fact confirms the role of resonance between vibrations with phonon of high densities and the splitting of 7F_0 to 7F_J levels, which should lead to much complex structure of the emission lines. Inspection of the excitation spectra in UV region at room and 77 K temperatures shows that some lines vanished upper 5L_6 level at room temperature (Fig. 4). Since often charge-transfer (CT) transitions play an important role in deexcitation processes, probably this is the same case. At that point we should attempt to show at what energy the CT transitions appear in our systems and analyse the decay times of 5D_0 level of Eu^{3+} in the systems under investigations.

4. Conclusions

1. The X-ray data of binuclear title compounds prove the creation of Ln-Hg pseudodimer systems, where the metals are connected through two SCN bridging ligands bonded by N and S atoms to Eu and Hg ones, respectively. Neodymium ion is coordinated with four Hmpa molecules and two types of SCN⁻ ions, two of them being bridging ligands, and one monodentate.

2. Asymmetric arrangements in sevenfold coordination of lanthanide ions, where the ligands have different polarizabilities, result in unexpectedly low hypersensitive transition intensities.
3. Markedly strong vibronic coupling with ν_{PO} and ν_{CN} modes were detected.
4. Significant emission intensities were recorded both at 293 and 77 K in the europium binuclear compound.

Acknowledgments

This work was sponsored by the Committee for Scientific Research.

References

- [1] J. Legendziewicz, *J. Appl. Spectrosc.* **62**, 192 (1995).
- [2] J. Legendziewicz, G. Oczko, E. Huskowska, *Bull. Acad. Sci. Pol. Chem.* **42**, 341 (1994).
- [3] T. Głowiak, J. Legendziewicz, E. Huskowska, P. Gawryszewska, *Polyhedron*, in press.
- [4] J. Legendziewicz, Z. Ciunik, P. Gawryszewska, J. Sokolnicki, *J. Alloys Comp.* **225**, 372 (1995).
- [5] V.V. Skopenko, V.M. Amirkhanov, *Dokl. Akad. Nauk Ukr. SSR, Ser. B* **8**, 49 (1986).
- [6] E. Gałdecka, Z. Gałdecki, V.M. Amirkhanov, J. Legendziewicz, in preparation.
- [7] V.M. Amirkhanov, A.A. Kapshuk, F.G. Kramarenko, V.V. Skopenko, *Russian J. Inorg. Chem.* **39**, 1101 (1994).
- [8] L. Macalik, J. Hanuza, J. Sokolnicki, J. Legendziewicz, *J. Appl. Spectrosc.* **62**, 40 (1995).