Russian Journal of Coordination Chemistry, Vol. 27, No. 10, 2001, pp. 746–750. Translated from Koordinatsionnaya Khimiya, Vol. 27, No. 10, 2001, pp. 790–794.
Original Russian Text Copyright © 2001 by Karasev, Petrochenkova, Mirochnik, Petukhova, Lifar.

Influence of the Nature of Carboxylic Acid on the Luminescence and Spectral Properties of (Carboxylato)bis(dibenzoylmethanato)europium(III) Complexes

V. E. Karasev, N. V. Petrochenkova, A. G. Mirochnik, M. V. Petukhova, and L. I. Lifar

Institute of Chemistry, Far East Division, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia

Received August 21, 2000

Abstract—A series of (carboxylato)bis(dibenzoylmethanato)europium(III) complexes containing anions of both saturated and unsaturated carboxylic acids were synthesized to compare the luminescence and spectral properties of heteroligand Eu(III) complexes. (Carboxylato)bis(dibenzoylmethanato)europium(III) complexes with unsaturated acid anions were synthesized for the first time. The compounds obtained were characterized using elemental analysis and luminescence and IR spectroscopy. These studies revealed two types of influence of the nature of an acid substituent on the luminescence spectra of (carboxylato)bis(dibenzoylmethanato)europium(III) complexes. The anomalous Stark structure of the luminescence spectra of one group of compounds is attributed to the charge transfer state at 77 K.

The creation of light-collecting and light-transforming composite materials, including those produced from macromolecular complexes (MMCs), is of topical interest. Metal-containing polymers with various chromophores can be prepared, e.g., through polymerization and copolymerization of metal-containing monomers [1, 2].

Previously [3, 4], we studied the luminescence and spectral properties and polymerization transformations of Ln(III) salts with unsaturated acids and of the derived heteroligand complexes. Insofar as the fluorescence intensity of the lanthanide ions in MMC is low, study of the energy migration in lanthanide-containing monomers and in MMCs and the search for methods of sensitizing the fluorescence of Ln^{3+} are topical problems. Dibenzoylmethane $C_6H_5CO(CH_2)COC_6H_5$ (HDbm) is known to possess a branched π electron system, which can favor fluorescence sensitization.

In continuation of the studies into the influence of the composition and structure of starting metal-containing monomers on the fluorescence of MMC, as well as for the purpose of comparing the luminescence and spectral properties of heteroligand complexes containing saturated [5, 6] and unsaturated carboxylic acids, we investigated the luminescence and spectral properties of some (carboxylato)bis(dibenzoylmethanato)europium(III) complexes $Eu(Dbm)_2Acid \cdot nH_2O$ (where Acid is the acrylate (Acr^-), methacrylate ($Macr^-$), cinnamate (Cin^-), α-cyano-β-phenylacrylate ($CN\text{-}Cin^-$), β-piperanylacrylate ($\beta\text{-}Pipacr^-$), formate ($Form^-$), acetate (Ac^-), trifluoroacetate ($TFAc^-$), propionate ($Prop^-$), butyrate (But^-), valerate (Val^-), isovalerate ($Isoval^-$), caproate (Hex^-), and caprylate (Oct^-) anions, and $n = 0$, 0.5, and 1). Note that the (carboxylato)bis(dibenzoylmethanato)europium(III) complexes with the unsaturated acid anions $TFAc^-$ and $Form^-$ were obtained for the first time.

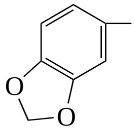
EXPERIMENTAL

Unlike (carboxylato)(β-diketonato)europium(III) complexes [5], the $Eu(Dbm)_2Acid \cdot nH_2O$ complexes ($n = 0$, 0.5, and 1) were synthesized in one step by reacting stoichiometric amounts of $Eu(NO_3)_3 \cdot 6H_2O$, the corresponding acid, and HDbm in a small amount of ethanol with continuous stirring. The reaction mixture was neutralized with ethanolic ammonia, and the resulting precipitate was filtered off, washed with ethanol, and dried in air and *in vacuo*. For example, $Eu(Dbm)_2Acr \cdot 0.5H_2O$ was prepared as follows. $Eu(NO)_3 \cdot 6H_2O$ (0.0024 mol) was dissolved under heating in 20 ml of ethanol, and HDbm (0.0012 mol) was added. Then, HAcr (0.0012 mol) was added dropwise with continuous stirring. The reaction mixture was neutralized by adding a concentrated solution of ammonia in drops with stirring until a voluminous powdery precipitate of $Eu(Dbm)_2Acr \cdot 0.5H_2O$ was formed. The precipitate was filtered off, washed repeatedly with ethanol, and dried in air and then *in vacuo* at 60°C.

All of the (carboxylato)bis(dibenzoylmethanato)europium(III) complexes are yellow powders and are insoluble in water and nonpolar organic solvents but soluble in hot DMF, DMSO, dioxane, and cyclohexanone under heating.

The compounds obtained were characterized using elemental analysis (Table 1) and IR and luminescence spectroscopy. IR spectra were recorded on a Perkin-Elmer Spectrum-1000 spectrophotometer (KBr) in the

Table 1. Elemental analysis data for the $Eu(Dbm)_2RCOO \cdot nH_2O$ complexes

No.	R		*n*	Empirical formula	Content (found/calculated), %			
					C	H	N	Eu
I	$CH_2{=}CH$	(Acr)	0.5	Eu $C_{33}H_{26}O_{6.5}$	57.94/58.04	4.06/3.83		22.33/22.41
II	$CH_2{=}C(CH_3)$	(Macr)	0.5	Eu $C_{34}H_{28}O_{6.5}$	58.72/58.87	4.00/3.89		22.00/21.93
III	Ph–CH=CH	(Cin)	0.5	Eu $C_{39}H_{30}O_{6.5}$	61.86/61.99	4.21/4.10		20.01/20.13
IV	 CO−CH=CH	(β-Pipacr)		Eu $C_{41}H_{30}O_9$	61.70/61.65	4.11/4.01		19.80/19.05
V	Ph–CH=C(CN)	(CN-Cin)	0.5	Eu $C_{40}H_{29}O_6N$	61.84/61.53	4.05/3.84	1.80/1.79	19.70/19.48
VI	H	(Form)		Eu $C_{31}H_{23}O_6$	57.89/57.85	3.56/3.42		23.80/23.64
VII	CF_3	(TFAc)	1	Eu $C_{32}H_{24}O_7F_3$	52.52/52.60	3.39/3.56		20.47/20.82
VIII	CH_3	(Ac)		Eu $C_{32}H_{25}O_6$	58.46/58.44	3.78/3.81		23.00/23.14
IX	C_2H_5	(Prop)		Eu $C_{33}H_{27}O_6$	58.46/59.02	3.99/4.02		22.48/22.65
X	C_3H_7	(But)		Eu $C_{34}H_{29}O_6$	59.53/59.56	4.59/4.23		22.30/22.16
XI	C_4H_9	(Val)		Eu $C_{35}H_{31}O_6$	61.75/61.80	4.50/4.43		21.98/21.75
XII	*i*-C_4H_9	(Isoval)		Eu $C_{35}H_{31}O_6$	61.98/61.80	4.64/4.43		22.00/21.75
XIII	C_5H_{11}	(Hex)		Eu $C_{36}H_{33}O_6$	60.23/60.59	4.60/4.63		21.03/21.32
XIV	C_7H_{15}	(Oct)		Eu $C_{38}H_{37}O_6$	61.56/61.54	4.91/4.99		20.38/20.51

range 400–4000 cm^{-1}. Luminescence spectra were recorded on a SDL-1 spectrometer with a DRSh-250 mercury lamp as an excitation source. Luminescence excitation spectra were recorded on a setup based on the SDL-1 spectrometer and an MRD-23 monochromator with a Tungsram xenon lamp (2500 W) as an excitation source. Measurements were carried out at 300 and 77 K.

RESULTS AND DISCUSSION

The IR spectra of the (carboxylato)bis(dibenzoylmethanato)europium(III) complexes obtained are alike. They all show a set of intense absorption bands at 550–900 and 1380–1597 cm^{-1}. These bands cannot be precisely assigned because the CO and phenyl stretching vibrations in dibenzoylmethane, as well as $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ in the acid, overlap.

The intense band at 1552 cm^{-1} corresponds to ν(C=O) of Dbm^- [7]. The benzene rings of Dbm^- give bands at 1480 and 1597 (ν(C=C)) and 1070 cm^{-1} (in-plane deformation vibrations) and medium-intensity bands at 686, 720, 750, and 784 $^{-1}$ (out-of-plane deformation vibrations). The positions and intensities of these bands in the spectra of (carboxylato)bis(dibenzoylmethanato)europium(III) complexes are very close to those in the IR spectrum of dibenzoylmethanatoeuropium(III).

The carboxylate anions in complexes **I**–**XIV** give a new band at 1520 cm^{-1} ($\nu_{as}(COO^-)$) and a doublet at 1380–1400 cm^{-1}, a component of which is due to $\nu_s(COO^-)$. The difference between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ frequencies (~130 cm^{-1}) suggests a bridging bidentate coordination of the carboxyl groups by the europium atom [8].

The IR spectra of **I**–**III**, **V**, and **VII** show bands at 3300–3400 cm^{-1} from the stretching vibrations of water. The presence of crystallization water in these compounds is also confirmed by thermogravimetric measurements (elimination of the water molecules occurs below 100°C).

The antisymmetrical and symmetrical CH_3 and CH_2 stretching vibrations give bands at 2850–2950 cm^{-1}. Their intensities in the spectra of compounds **VIII**–**XIV** depend on the number of skeletal carbon atoms in the corresponding acid. The intensities of the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ bands (at 2926 and 2850 cm^{-1}, respectively) increase when passing from (acetato)bis(dibenzoylmethanato)europium(III) to (caprylato)bis(dibenzoylmethanato)europium(III).

The IR spectra of **I**–**V** and **VII** contain bands characteristic of the corresponding substituents in R. Thus, the spectra of $Eu(Dbm)_2Cin \cdot 0.5H_2O$, $Eu(Dbm)_2(CN\text{-}Cin) \cdot 0.5H_2O$, and $Eu(Dbm)_2$(β-Pipacr) show broadened bands from the benzene ν(C=C) vibrations; in addition, bands at 1070, 784, and 750 cm^{-1} corresponding to the benzene δ(CH) vibrations become more intense and split into two components. The intensity of the band at 3060 cm^{-1} (the ν(CH) vibrations of the benzene ring) also increases. The spectrum of$Eu(Dbm)_2(CN\text{-}Cin) \cdot 0.5H_2O$ contains a weak ν(CN)

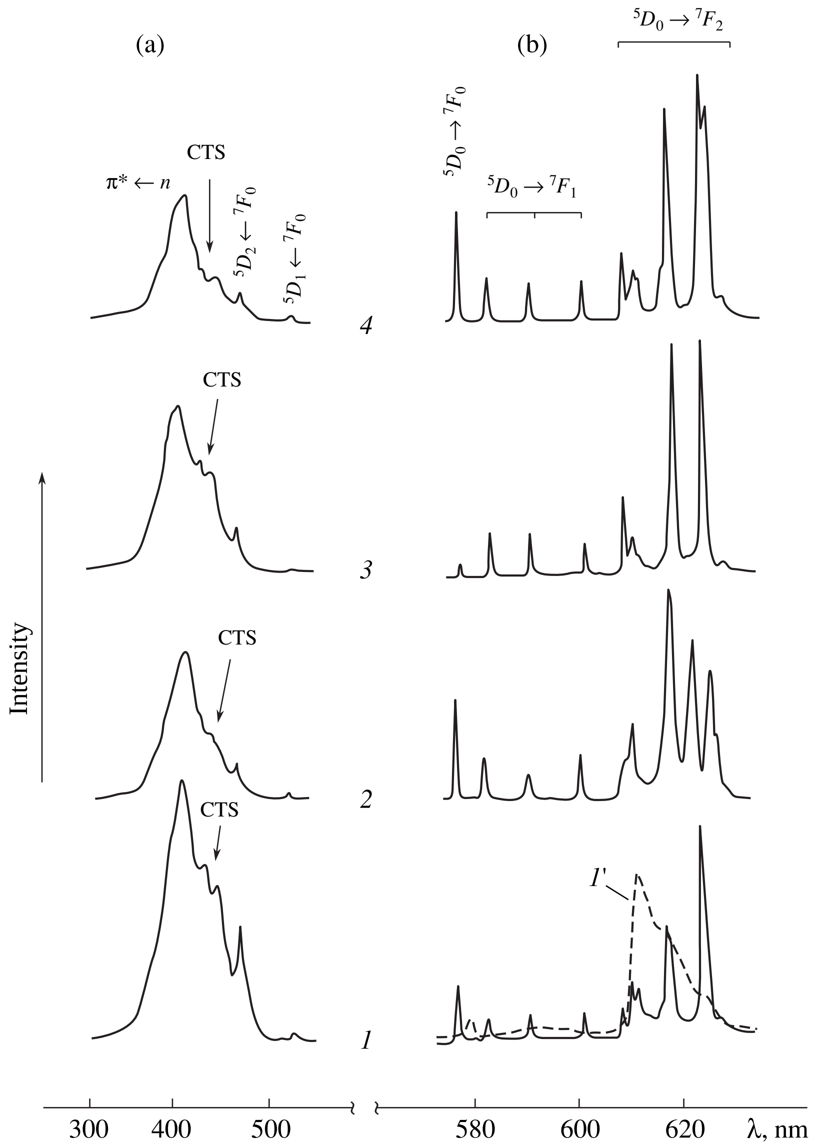


Fig. 1. (a) Luminescence excitation spectra (λ_{lum} = 615 nm, 77 K) and (b) luminescence spectra (77 K) of (*1*, *1*' (300 K)) $Eu(Dbm)_2Acr \cdot 0.5H_2O$, (*2*) $Eu(Dbm)_2Macr \cdot 0.5H_2O$, (*3*) $Eu(Dbm)_2Cin \cdot 0.5H_2O$, and (*4*) $Eu(Dbm)_2Oct$.

band at 2222 cm^{-1} [8]. The IR spectrum of $Eu(Dbm)_2$(β-Pipacr) exhibits additional bands at 1252 (s) and 1041 cm^{-1} (m) attributable to the ν(=C–O–) and ν(C–O–C) vibrations of the piperanyl group. In the IR spectrum of $Eu(Dbm)_2(TFAc) \cdot H_2O$, a $\nu(CF_3)$ band appears at 1200 cm^{-1}. The spectra of complexes **I**–**V** that contain an unsaturated acid anion show a band at 1640 cm^{-1} corresponding to the ν(C=C) vibrations of the acid. The deformation and stretching vibrations of the chelating M–O bond give bands in the range below 650 cm^{-1}.

The (carboxylato)bis(dibenzoylmethanato)europium(III) complexes obtained exhibit bright luminescence at 77 K. Based on their luminescence spectra, one can divide these compounds into two groups. The first group includes complexes **I**–**IV** and **VIII**–**XIV**, whose luminescence spectra (Fig. 1b) differ significantly in band splitting and intensity distribution from those of most of the known Eu(III) complexes and are similar to the spectra of the previously studied (carboxylato)(dibenzoylmethanato)europium(III) complexes [5].

In the spectra of these compounds, the $^5D_0$–$^7F_0$ singlet-singlet transition is more intense than the $^5D_0$–$^7F_1$ one. The Stark components of the $^5D_0$–$^7F_1$ transition are spaced apart at a long distance; the splitting value ΔF_1 is nearly the same for all complexes of this group (17.3–18.8 nm). The $^5D_0$–$^7F_2$ transition band contains up to seven components, which can be subdivided into three groups depending on their intensities. Note that the acid structure (the presence of substituents and the hydrocarbon radical length) most strongly influences the redistribution of the intensities of the $^5D_0$–$^7F_2$ transition bands in the range 607–612 nm, in which two to four bands of different intensity can appear (Fig. 1b)

The luminescence spectra of the complexes belonging to the second group (**V**–**VII**) are close to those of most Eu(III) chelate complexes [9]. The $^5D_0$–$^7F_2$ transition accounts for the major fraction of emission energy, the intensity of the $^5D_0$–$^7F_0$ transition being insignificant (Fig. 2b). The ΔF_1 value is nearly constant for the compounds of this group (7.9–8.4 nm).

The relative luminescence intensities I_{fl} for the obtained Eu(III) complexes at 77 and 300 K are presented in Table 2. The I_{fl} value for Eu(Dbm)$_2$Hex at 300 K was taken as an arbitrary unit. It can be seen that Eu(Dbm)$_2$Oct (77 K) has the highest I_{fl} value among the compounds under study. The intensity I_{fl} increases with the carbon chain length in the order **VIII**–**XI** and then from **XIII** to **XIV**.

The changes in the luminescence and spectral properties of the compounds under discussion are most probably associated with the nature of substituents R in RCOO$^-$. The electron influence of the substituents on the reaction centers in like organic ligands can be characterized by an inductive constant of substituents σ^* (the Taft constant) [10]. It is known that σ^* serves as a measure of the inductive effect, as it is proportional to the electron density redistribution on a reaction center caused by substituents [11]. The second group includes the Eu(Dbm)$_2$Acid · nH$_2$O complexes in which Acid$^-$ has substituents with a strong negative inductive effect (CN, CF$_3$, and H). In the diffuse luminescence spectra of these compounds (**V**–**VII**), I_{fl} decreases with an increase in σ^* (Table 2), while the spectra of the complexes with a weak negative (CH=CH, C$_6$H$_5$, and CH=CH$_2$) or positive inductive effect (CH$_3$, C$_2$H$_5$, etc.) of the acid substituent have a discrete character. In the series of compounds **VIII**–**XIV**, I_{fl} increases with a decrease in σ^*.

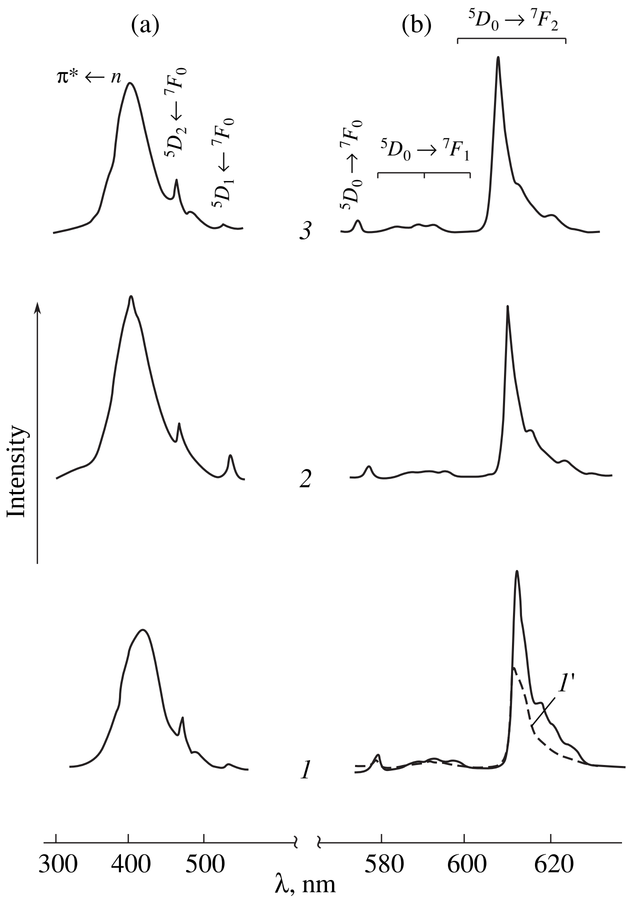


Fig. 2. (a) Luminescence excitation spectra (λ_{lum} = 615 nm, 77 K) and (b) luminescence spectra (77 K) of (*1*, *1'* (300 K)) Eu(Dbm)$_2$(CN-Cin) · 0.5H$_2$O, (*2*) Eu(Dbm)$_2$Form, and (*3*) Eu(Dbm)$_2$(TFAc) · H$_2$O.

The luminescence spectra of the complexes belonging to the first group (**I**–**IV** and **VIII**–**XIV**) have anomalous Stark structures characterized by an unusually high luminescence intensity of the singlet-singlet $^5D_0$–$^7F_0$ transition and by a large Stark splitting Δ^7F_1. Such a distribution of the luminescence intensity cannot be explained by the Judd–Ofelt theory and seems to be due to a partially borrowed intensity from the charge trans-

Table 2. Relative luminescence intensity of the (carboxylato)bis(dibenzoylmethanato)europium(III) complexes at 77 and 300 K and the Taft constants σ^* for the acid substituents

Compound	I_{fl}, arbitrary units		σ^* [10]	Compound	I_{fl}, arbitrary units		σ^* [10]
	77 K	300 K			77 K	300 K	
I	3876	34	+0.40	**VIII**	3957	2	0.00
II	4926	48		**IX**	5634	4	–0.100
III	6922	4	+0.41	**X**	6346	19	–0.115
IV	2667	1		**XI**	7370	2	–0.130
V	2774	132		**XII**	5664	37	–0.125
VI	4334	363	+0.49	**XIII**	6662	1	–0.162
VII	4489	609	+2.60	**XIV**	7385	1	

fer band [9]. The formation of charge transfer complexes at 77 K for the compounds of the first group is indicated by the presence of a long-wave component at 420–460 nm in their luminescence excitation spectra (Fig. 1a). This band is absent from the luminescence excitation spectra of compounds **V**–**VII**, which constitute the second group (Fig. 2a), and from those of the first group compounds at 300 K, suggesting that the formation of the charge transfer state in the ligand–metal system at 77 K is favored by acid substituents with a positive inductive effect in the latter complexes.

The behavior of compounds in both groups is different at 300 K. In the first group (complexes **I**–**IV** and **VIII**–**XIV**), luminescence is quenched almost completely (the intensity decreases by more than a hundred times). In addition, the spectral pattern changes significantly at 300 K, approximating that of complexes **V**–**VII** (the second group) and of most Eu(III) chelates. The luminescence intensity of the second group compounds is reduced by less than ten times, and the spectral pattern changes only slightly (Table 2, Figs. 1b, 2b). Almost completely quenched (“switched off”) luminescence at 300 K indicates the formation of a new effective mechanism for the degradation of electron excitation energy.

This study revealed two types of influence of the nature of a substituent in a carboxylic acid on the luminescence spectra of (carboxylato)bis(dibenzoylmethanato)europium(III) complexes. The anomalous Stark structure of the luminescence spectra of the compounds belonging to the first group is attributed to the charge transfer complexes formed at 77 K.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 98-03-32472a.

REFERENCES

1. Pomogailo, A.D. and Savost’yanov, V.S., *Metallosoderzhashchie monomery i polimery na ikh osnove* (Metal-Containing Monomers and Derived Polymers), Moscow: Khimiya, 1988.
2. Pomogailo, A.D. and Savost’yanov, V.S., *Usp. Khim.*, 1991, vol. 60, no. 7, p. 1513.
3. Petrochenkova, N.V., Petukhova, M.V., Mirochnik, A.G., and Karasev, V.E., *Koord. Khim.*, 2000, vol. 26, no. 5, p. 396.
4. Petrochenkova, N.V., Mirochnik, A.G., and Karasev, V.E., *Koord. Khim.*, 1991, vol. 17, no. 11, p. 1570.
5. Karasev, V.E., Steblevskaya, N.I., Vovna, I.V., and Shchelokov, R.N., *Zh. Neorg. Khim.*, 1982, vol. 27, no. 4, p. 904.
6. Mirochnik, A.G., Polyakova, N.V., and Karasev, V.E., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 12, p. 2559.
7. Bellamy, L.J., *Advances in Infrared Group Frequencies*, London: Chapman and Hall, 1968. Translated under the title *Novye dannye po IK-spektram slozhnykh molekul*, Moscow: Mir, 1971.
8. Karraker, D.G., *J. Inorg. Nucl. Chem.*, 1969, vol. 31, no. 9, p. 2815.
9. Gaiduk, M.I., Zolin, V.F., and Gaigerova, L.S., *Spektry lyuminestsentsii evropiya* (Luminescencse Spectra of Europium), Moscow: Nauka, 1974, p. 148.
10. Zhdanov, Yu.A. and Minkin, V.I., *Korrelyatsionnyi analiz v organicheskoi khimii* (Correlation Analysis in Organic Chemistry), Rostov-on-Don: Rostov. Gos. Univ., 1966.
11. Vereshchagin, A.N., *Induktivnyi effekt* (Inductive Effect), Moscow: Nauka, 1987.