INVESTIGATION OF COMPLEXES OF THE LANTHANIDES WITH BARBITURATES*

M. D. Pundlik and V. Ramachandra Rao

UDC 549.49:547.256.5'854.5:
543.422.4.5.6

New complexes of some lanthanides with barbiturates such as phenobarbital, amylbarbital, and butabarbital were obtained. Mixed complexes containing, in addition to the barbiturates, 8-hydroxyquinoline as a second ligand were also obtained. The complexes were characterized by their absorption spectra in the UV, visible, and the IR regions. Simple and mixed neodymium complexes with barbiturates were subjected to thermal analysis, and the results are discussed.

The study of complexes of barbiturates with transition elements is far from complete. Only copper [1,2], zinc, mercury, and nickel [2] complexes with barbiturates have been described.

Barbiturates are known mainly because of their soporific action, and the methods used to identify them by complexing with transition metals are of substantial analytical value [3]. However, complexes of the lanthanides have not been adequately studied, and methods for the preparation of complexes of the lanthanides with barbiturates and their mixed complexes with 8-hydroxyquinoline, as well as their spectral and thermal characteristics, were therefore investigated in detail in the present research.

EXPERIMENTAL

The spectroscopically pure lanthanide oxides used in this research were obtained from the Bhabha Center of Atomic Research in Bombay.

The UV and visible spectra were recorded with a Beckmann DB spectrophotometer. The IR spectra of mineral oil suspensions or KBr pellets of the compounds were recorded with Perkin–Elmer model 137 and 238 spectrometers.

The barbiturates of the lanthanides were obtained by the method in [4]. The excess ligand was washed away with ether. All of the compounds (Table 1) were vacuum dried over fused calcium chloride for 48 h.

The mixed complexes were obtained as follows. Solutions of the lanthanide barbiturate complex and 8-hydroxyquinoline in ethanol (molar ratio 1:3) were mixed, the pH of the solution was brought up to 5.8 by means of alcoholic ammonia solution, and the solution was evaporated slowly to dryness on a steam bath. The solid residue was washed with ether to remove the excess oxine (8-hydroxyquinoline) and vacuum evaporated over fused $CaCl_2$ for 48 h. The analytical data for the mixed complexes are presented in Table 2.

RESULTS AND DISCUSSION

Ultraviolet Region

The spectra of the complexes were recorded only in methanol solution because of their insolubility in other nonaqueous solvents. At pH values below 10 the barbiturates do not have any characteristic absorption in the UV region [3]. No selective absorption of the lanthanide complexes in methanol whatsoever was therefore observed.

---

*All inquiries should be directed to V. Ramachandra Rao.

Regional Engineering College, Visvesvaraya, Nagpur, India. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 837-844, June, 1976. Original article submitted July 29, 1975.

TABLE 1. Analytical Data for Lanthanide Complexes with Barbiturates

Complex*	Found, %			Calculated, %		
	metal	Cl	N	metal	Cl	N
$\mathrm{Y(phenobarb)_1Cl_3\cdot H_2O}$	19.76	24,02	6.20	19.99	23,72	6.28
$\mathrm{La(phenobarb)_1Cl_3\cdot H_2O}$	27,73	21,43	5.42	27.96	21,36	5.66
$\mathrm{Pr(phenobarb)_1Cl_3\cdot H_2O}$	27.90	20.96	5,50	28.37	21.24	5,63
$\mathrm{Nd(phenobarb)_1Cl_3\cdot H_2O}$	28,87	20.97	5,40	28.85	21,10	5.59
$\mathrm{Sm(phenobarb)_1Cl_3\cdot H_2O}$	29.52	20,54	5,46	29,71	20.84	5.52
$\mathrm{Gd(phenobarb)_1Cl_3\cdot H_2O}$	30,34	20,32	5.26	30.65	20.56	5.45
$\mathrm{Dy(phenobarb)_1Cl_3\cdot H_2O}$	31,22	20.10	5.37	31.36	20.35	5,39
$\mathrm{Y(amylobarb)_1Cl_3\cdot H_2O}$	19,99	24,13	6,16	20.22	24.22	6,37
$\mathrm{La(amylobarb)_1Cl_3\cdot H_2O}$	28,07	21,45	5.71	28.23	21.79	5.73
$\mathrm{Pr(amylobarb)_1Cl_3\cdot H_2O}$	29.56	22.23	5.40	29.75	22,49	5,72
$\mathrm{Nd(amylobarb)_1Cl_3\cdot H_2O}$	30.00	22,03	5,57	30.30	22.16	5,66
$\mathrm{Sm(amylobarb)_1Cl_3\cdot H_2O}$	29.93	21.15	5,33	30.01	21,25	5.59
$\mathrm{Y(butabarb)_1Cl_3\cdot H_2O}$	20.50	24,86	6,29	20,89	25.03	6.57
$\mathrm{La(butabarb)_1Cl_3\cdot H_2O}$	28,90	22,17	5,87	29,08	22,44	5.90
$\mathrm{Pr(butabarb)_1Cl_3\cdot H_2O}$	29.30	22.14	5.74	29,51	22,30	5,86
$\mathrm{Nd(butabarb)_1Cl_3\cdot H_2O}$	29.92	21.90	5,74	30,07	22.16	5,83
$\mathrm{Sm(butabarb)_1Cl_3\cdot H_2O}$	30,52	21,46	5,48	30,89	21,87	5,74
$\mathrm{Gd(butabarb)_1Cl_3\cdot H_2O}$	31.53	21,20	5.60	31,85	21,59	5,67
$\mathrm{Dy(butabarb)_1Cl_3\cdot H_2O}$	33,40	21.08	5,55	33.79	21,34	5.61

*Abbreviations: phenobarb is phenobarbital, amylobarb is amylbarbital, and butabarb is butabarbital.

TABLE 2. Analytical Data for Mixed Complexes

Complex*	Found, %			Calculated, %		
	metal	Cl	N	metal	Cl	N
$\mathrm{Y(phenobarb)_1(oxine)_2Cl\cdot H_2O}$	13,21	5,20	8.20	13,38	5,34	8.43
$\mathrm{La(phenobarb)_1(oxine)_2Cl\cdot H_2O}$	19,20	4,72	7.83	19.34	4.98	7,85
$\mathrm{Nd(phenobarb)_1(oxine)_2Cl\cdot H_2O}$	19,72	4,94	7.68	20,04	4.93	7.78
$\mathrm{Sm(phenobarb)_1(oxine)_2Cl\cdot H_2O}$	20.42	4,72	7,50	20.71	4.89	7.71
$\mathrm{Gd(phenobarb)_1(oxine)_2Cl\cdot H_2O}$	21,23	4.70	7.48	21.45	4.84	7.61
$\mathrm{Y(amylobarb)_1(oxine)_2Cl\cdot H_2O}$	13,41	5.02	8,05	13.50	5,37	8,50
$\mathrm{La(amylobarb)_1(oxine)_2Cl\cdot H_2O}$	19,22	4,90	7.80	19.50	5.01	7,91
$\mathrm{Pr(amylobarb)_1(oxine)_2Cl\cdot H_2O}$	19.70	4.81	7.70	19.83	4.99	7,87
$\mathrm{Nd(amylobarb)_1(oxine)_2Cl\cdot H_2O}$	20.01	4.95	7.75	20.19	4.97	7.84
$\mathrm{Sm(amylobarb)_1(oxine)_2Cl\cdot H_2O}$	20.84	4.80	7.63	20.88	4.93	7.77
$\mathrm{Y(butabarb)_1(oxine)_2Cl\cdot H_2O}$	13.77	5,49	8.40	13.79	5.50	8.69
$\mathrm{La(butabarb)_1(oxine)_2Cl\cdot H_2O}$	19.45	5.11	8.06	19.90	5.12	8.07
$\mathrm{Pr(butabarb)_1(oxine)_2Cl\cdot H_2O}$	20.14	5.09	7.94	20.23	5.10	8.04
$\mathrm{Nd(butabarb)_1(oxine)_2Cl\cdot H_2O}$	20.43	5.05	7.89	20.61	5.07	8.00
$\mathrm{Sm(butabarb)_1(oxine)_2Cl\cdot H_2O}$	21.22	4.97	7.80	21.30	5.02	7.93
$\mathrm{Gd(butabarb)_1(oxine)_2Cl\cdot H_2O}$	21.99	4.90	7.70	22.12	4.99	7.87
$\mathrm{Dy(butabarb)_1(oxine)_2Cl\cdot H_2O}$	22.41	4,63	7,75	22.63	4.94	7.80

*Abbreviations: phenobarb is phenobarbital, amylobarb is amylbarbital, butabarb is butabarbital, and oxine is 8-hydroxyquninoline.

A study of the spectra of mixed complexes with 8-hydroxyquinoline showed that the characteristic absorption maxima of 8-hydroxyquinoline that are observed at 240 and 320 nm are retained without specific changes for the mixed lanthanide–phenobarbital–8-hydroxyquinoline complexes, except for an additional band at 255 nm in the spectra of the neodymium, samarium, and gadolinium complexes. With the exception of the neodymium complex, the band at 320 nm is absent in the spectra of all of the amylbarbital-8-hydroxyquinoline complexes. The band at 320 nm is absent in all cases in the spectra of the mixed butabarbital–8-hydroxyquinoline complexes, whereas an additional band at 260 nm appears in the spectra of the lanthanum, praseodymium, samarium, and gadolinium complexes. Despite the fact that the usually higher absorption of the ligand as compared with the metal ion masks any splitting of the bands, the presence of an additional band at 255 nm in the spectra of these complexes could be due to splitting of the band at 240 nm characteristic for 8-hydroxyquinoline. The log ε values of the lanthanide–barbiturate–8-hydroxyquinoline complexes range from 3.25 to 5.16.

Visible Region

A study of the spectra in the visible region gives information relative to the changes in the intensities, shifts, and splittings of the bands [4-8].

The absorption bands at 444 and 480 nm in the spectra of the praseodymium–barbiturate complexes are characterized by a small red shift and a change in the intensity. An absorption band at 590 nm is observed only in the case of the phenobarbital complex.

TABLE 3. Absorption Bands (in cm^{-1}) in the IR Spectra of Lanthanide Complexes with Barbiturates

Ligand	Y complex	La complex	Pr complex	Nd complex	Sm complex	Gd complex	Dy complex	Assignment
Phenobarbital								
	3650 w					3600 w	3650 w	Water OH
	3425 w					3390 w	3400 w	
3290 s	3250 w	3200 w	3220 m	3200 w	3210 w		3250 w	NH stretching vibrations
3160br, m		1710 m	1710 s	1705 s	1710br, s	1705 s	1720 s	C = O in the 4 and 6 positions
1725 w								
1700 w	1675 m	1695 m	1680 m	1680 w	1680 w	1680 w		
1670 m			1670 m	1665 m	1670 w		1670 w	C = O in the 2 position
1660 s		1620 br, m	1635 br, m	1630 m	1640 w			
Amylbarbital								
3150 w	3180 m	3160 m	3150 m	3150 m	3130 w			NH stretching vibrations
1725 s	1725 s	1720 s	1720 s	1705 s	1710 s			C = O in the 4 and 6 positions
1680 s	1680 s	1680 s	1680 s	1690 s	1680 s			C = O in the 2 position
	1625 m	1610 sh	1625 m		1610 w			
Butabarbital								
	3575 w	3600 m		3600 m	3590 m	3550 m	3550 m	Water OH
	3325 m	3350 m	3290 w	3350 s	3350 s	3310 m	3350 m	NH stretching vibrations
3125 br, s	3110 m	3125 w	3150 sh	3150 s	3110 s	3100 m	3150 m	C = O in the 4 and 6 positions
1720 sh	1725 s	1725 s	1725 s	1725 s	1725 s		1725 s	
1710 sh						1710 s		C = O in the 2 position
1675 s	—	—	—	—	—	—	—	

The characteristic bands of the Nd^{3+} ion in the spectrum of the neodymium–phenobarbital complex are characterized by a red shift and a large increase in the ε value. Only the band at 576 nm in the spectrum of the amylbarbital complex displays a red shift to 586 nm. In the spectrum of the butabarbital complex only the characteristic bands at 521 and 576 nm are shifted to the red region and are observed at 525 and 585 nm, respectively; a pronounced increase in the absorption is noted.

Splitting of the characteristic absorption band of the Sm^{3+} ion at 402 nm [7] was observed in the spectrum of the acetylacetonate complex of the Sm^{3+} ion, whereas splitting of this band was not observed in the case of complexes with other diketones [8] and many other samarium complexes [4, 9-13]. However, the absorption maximum in the spectrum of its complex with anthranilic acid [14] is characterized by a red shift. This absorption band was observed in the present research at 415 nm in the case of the phenobarbital complex and at 404 nm in the case of the butabarbital complex, whereas it vanished in the case of the amylbarbital complex. The red shift observed in the present research is comparable to the shift observed in the spectrum of samarium anthranilate.

In the case of the mixed complexes we were unable to observe any one of the characteristic bands of the Pr^{3+}, Nd^{3+}, and Sm^{3+} ions; this is apparently a consequence of the strong absorption of the 8-hydroxyquinoline fragment at 400-800 nm.

Some of the changes (the shift and the increase in the intensities) of the characteristic bands of the Pr^{3+}, Nd^{3+}, and Sm^{3+} ions that were observed in the visible region of the spectrum can be linked with dsp hybridization and also with the strong interaction of the metal ion with the ligands.

Infrared Region

The IR spectra of various barbiturates have been studied by several investigators [1, 15-17]. The position and the intensity of the absorption bands depend mainly on two factors: first, on the nature of the substituents in the 1 and 5 positions, and, second, on whether the barbiturate exists in the free acid form or in the sodium salt form. The spectra of all of the barbiturates contain two bands at 3100-3200 cm^{-1} (NH stretching vibrations) and several bands at 2800-300 cm^{-1} (C–H vibrations of the alkyl substituents).

TABLE 4. Absorption Bands (in cm^{-1}) in the IR Spectra of Mixed Complexes

Ligands		Y complex	La complex	Pr complex	Nd complex	Sm complex	Gd complex	Dy complex	Assignment
Pheno-barbital	Oxine								
		3800 br, m	3850 w		3750 w	3800 br	3850 m		Water OH
	3500–3300 br, m	3400 w	3450 w		3500 w	3450 m			Stretching vibrations of the phenolic OH group
3290 s		—	—	—	—	—	—		Stretching vibrations of the phenobarbital NH bond
3160 br, m									
1725 w		1725 m			1725 s	1725 s	1725 w		C = O groups in the 4 and 6 positions
1700 w			1705 s						
1670 m		—	—						C = O group in the 2 position of phenobarbital
1660 s	1090 w	1105 s	1105 s		1100 s	1110 s	1102s		Stretching vibrations of the oxine C–O bond
Amyl-barbital	Oxine								
	3500–3300 br, m	3400–3100 br, w	3400–3100 br, w	3400–3300 br, w	3400–3200 br	3400–3200 br			Stretching vibrations of the phenolic OH group
3150 w		—	—	—	—	—			Stretching vibrations of the phenobarbital NH bond
1725 s		1720 w	1710 br	—	1705 br, w	1705 br, w			C = O groups in 4 and 6 positions
1680 s		1680 w	1680 m	1680 w	1680 m	1675 m			C = O group in the 2 position of amylbarbital
		1640 w		1625 m	1615 br, w				
	1090 w	1090 m	1090 br, w	1090 s	1090 m	1085 m			Stretching vibrations of the oxine C–O bond
Buta-barbital	Oxine								
	3500–3300 br, m	3200–3100 s	3150 br, w	3500–3200 br, m	3150 br, m	3300–3100 br, m	3300 m	3200 m	Stretching vibrations of the phenolic OH group
3125 br, s		—	—	—	—	—	—	—	Stretching vibrations of the butabarbital NH bond
1720 sh			1710 sh		1710 s	1710 s	1710s	1720 s	C = O groups in 4 and 6 positions
1710 sh			1690 m	1690 m	1690 s	1690 s	1690s	1700 s	
1675 s		1670 m			—	—	—	—	C = O group in the 2 position of butabarbital
	1090 w	1105 s	1105 s	1100 s	1100 s	1100 s	1110s	1105 s	Stretching vibrations of the oxine C–O bond

The barbiturates have three groups of strong absorption bands at 1670-1765 cm^{-1}, which correspond to the stretching vibrations of the C=O groups and were investigated in detail in [16]. The first group of bands is observed at 1740-1760 cm^{-1} (the C=O groups in the 4 and 6 positions), the second group is observed at 1700-1720 cm^{-1} (C=O groups in the 4 and 6 positions, which experience the effect of the vibrations of the C=O group in the 2 position), and the third group is observed at 1670-1700 cm^{-1} (vibrations of the C=O group in the 2 position).

The various barbiturates investigated in the present research have absorption bands at 3125-3290 cm^{-1} that are related to the frequency of the NH stretching vibrations. Only one absorption band at 3200 cm^{-1} was observed in the spectra of the lanthanide–phenobarbital complexes. The frequency of the NH stretching vibrations in the series of lanthanide–amylbarbital complexes is changed somewhat, whereas the corresponding band in the spectra of the butabarbital complexes is split. The C–H absorption bands of the alkyl substituents are shifted and are observed at 2950-3080 cm^{-1}.

All three groups of bands of the carbonyl groups are observed in the spectra of the lanthanide–phenobarbital complexes. However, the characteristic frequency of the second group at 1725 cm^{-1} was observed between 1695 and 1710 cm^{-1} in the case of the free ligand. The vibrations of the C=O group in the 2 position, which were noted at 1670 cm^{-1} in the spectrum of the free ligand, are observed at 1620-1680 cm^{-1} in the spectra of most of the complexes. On the basis of these observations one can conclude that the C=O group in the 2 position is possibly involved in the formation of a bond. A similar phenomenon was also noted in the case of other complexes of barbiturates with lanthanides, except for the band at 1675 cm^{-1}, which was observed in the case of butabarbital but was absent in the spectra of all of the complexes. The spectral data for some of the lanthanide complexes with barbiturates are presented in Table 3.

Mixed Complexes

8-Hydroxyquinoline (oxine) has an absorption band at 3500 cm^{-1} (the stretching vibration of the phenolic OH group). This band is shifted in the spectra of some of the mixed barbiturate–8-hydroxyquinoline complexes, and this may be considered to be proof for the formation of an O–M bond. The shift in the stretching vibrations of the C–O bond from 1090 cm^{-1} for the C–OH group of oxine to 1100-1105 cm^{-1} in the spectra of all of the mixed complexes may also be another indication of the formation of an O–M bond.

The following conclusions can be drawn on the basis of a study of the IR absorption frequency of the barbiturates in the mixed complexes: 1) the bands of the stretching vibrations of the NH groups vanish or are shifted during complexing; 2) the bands of the stretching vibrations of the C=O group in the 2 position are absent in the spectra of the mixed butabarbital complexes, whereas they are shifted in the spectra of the mixed phenobarbital and amylbarbital complexes.

The data obtained in this study make it possible to assume that the C=O group in the 2 position of the barbiturates participates in complexing both in the case of simple complexes and mixed complexes. One of the nitrogen atoms (either in the 1 position or in the 3 position) is also involved in bond formation. Inasmuch as both nitrogen atoms are oriented symmetrically relative to the carbonyl group, it is difficult to draw a definite conclusion and state a preference for one of them.

The spectral data for the mixed complexes are presented in Table 4.

Thermal Decomposition of Simple and Mixed Neodymium-Barbiturate Complexes

The combined curves showing the weight loss (TG), thermal effect (DTA), and rate of change of the weight loss (DTG) were recorded for 200-mg samples, which were heated in a platinum crucible at 10 deg/min at atmospheric pressure in a stream of air. The three different neodymium–barbiturate complexes display weight losses of ~3% at 100-120°, and this was conjecturally linked to dehydration of the complex. An endothermic peak on the DTA curves was observed at 160-200° for all of the barbiturate complexes. In a communication regarding the thermogravimetric study of 5-nitrobarbituric acid [18] it was pointed out that this compound decomposes explosively at 185°. A comparison of barbituric and 5-nitrobarbituric acids makes it possible to consider the endothermic peak of the neodymium–barbiturate complexes at 200° to be, within a first approximation, the initial decomposition point.

The exothermic peak in the case of all of the complexes at 520° corresponds to a weight loss of 46-49%, and this indicates complete elimination of the ligand. A sesquioxide is formed at 800°, as indicated by the sloping portion of the TG curve in this region. The intermediate formation of a chloride cannot be postulated, inasmuch as there are no indications whatsoever of this on the TG curve. The overall process can be represented by the scheme

$$\mathrm{Nd}(L)_1\mathrm{Cl}_3\cdot \mathrm{H_2O} \rightarrow \mathrm{Nd}(L)_1\mathrm{Cl}_3 \rightarrow \mathrm{Nd_2O_3}.$$

The thermal decomposition of the mixed complexes exhibited a weight loss of 2% on the TG curve, and this constitutes evidence for a dehydration process. The endothermic peak at 200° on the DTA curve in the case of all of the mixed complexes may correspond to explosivelike decomposition of the barbituric acid, as in the case of simple barbiturate complexes. The other endothermic peak at 380-400° corresponds to a weight loss of 30-33%; this indicates initial splitting out of a barbiturate molecule.

A combined examination of the DTA and TD curves provides a basis for the assumption that one of the oxine molecules is lost at 600° and a second oxine molecule is lost at 800°. The calculated and experimentally observed weight losses indicate two-step elimination of the oxine molecules. A sesquioxide is formed finally at 900°. The decomposition can be depicted by the scheme

$$\mathrm{Nd}(L)_1(L')_2\mathrm{Cl}\cdot \mathrm{H_2O} \rightarrow \mathrm{Nd}(L)_1(L')_2\mathrm{Cl} \rightarrow \mathrm{Nd}(L')_2\mathrm{Cl} \rightarrow \mathrm{Nd}(L')\mathrm{Cl} \rightarrow \mathrm{Nd_2O_3}.$$

The authors thank the Director of the Research Institute (Vardkha) Dr. Shrivastava for making it possible to record the UV and visible spectra. They also thank R. S. Deindur for his assistance in the interpretation of the spectra. Thanks are also due to Dr. K. V. S. Krishnamurthy and M. George Wicks (Chemistry Department of Georgetown University, Washington, and Chemistry Department of Osman University) for recording the IR spectra. M. D. Pundlik thanks Dr. Z. M. Dokras, Director of the Laboratory of the Engineering College (Visvesvaraya, Nagpur) for the various possibilities offered. He also thanks the Director of the Laboratory of Forensic Sciences Dr. B. N. Matua and the Assistant Director of this laboratory Dr. S. K. Megkhal for their support.

LITERATURE CITED

1. L. Levy and C. E. Hubley, Anal. Chem., 28, 1591 (1956).
2. D. Tschan and K. Leupin, Pharm. Acta Helv., 42, 657 (1967); Chem. Abstr., 68, 6176 (1968).
3. E. G. C. Clarke, Isolation and Identification of Drugs, London (1969), p. 98.
4. Y. H. Deshpande and V. Ramachandra Rao, J. Inorg. Nucl. Chem., 35, 3626 (1973).
5. T. Moeller, J. Am. Chem. Soc., 72, 5447 (1950).
6. R. C. Vickery, J. Chem. Soc., 423 (1952).
7. T. Moeller and W. F. Ulrich, J. Inorg. Nucl. Chem., 2, 164 (1956).
8. D. Purushotham, V. Ramachandra Rao, and B. S. V. Raghav Rao, Anal. Chim. Acta, 33, 182 (1965).
9. P. Radhakrishna Murthy and V. Ramachandra Rao, Curr. Sci., 35, 12 (1966).
10. P. Radhakrishna Murthy, and V. Ramachandra Rao, Curr. Sci., 36, 223 (1967).
11. P. Radhakrishna Murthy and V. Ramachandra Rao, Indian J. Chem., 6, 465 (1968).
12. P. V. Tavalkar and V. Ramachandra Rao, Indian J. Chem., Vol. 7, 943 (1969).
13. S. Fazal Mehidi Ali and V. Ramachandra Rao, J. Inorg. Nucl. Chem. (in Press).
14. Y. H. Deshpande and V. Ramachandra Rao, Indian J. Chem., 7, 1051 (1969).
15. C. J. Umberger and G. Adams, Anal. Chem., 24, 1309 (1952).
16. W. C. Price, J. E. S. Bradley, R. D. B. Fraser, and J. P. Quilliam, J. Pharm. Pharmac., 6, 522 (1954).
17. L. G. Chatten and L. Levy, Appl. Spectroscop., 11, 177 (1957).
18. A. Berlin, M. E. Taylor, and R. J. Robinson, Anal. Chim. Acta, 24, 427 (1961).