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MAGNETIC STUDY IN SOLUTION OF LANTHANIDE(III)-BISMUTH(III) COORDINATION COMPOUNDS BY MEANS OF NMR SPECTROSCOPY

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NMR spectroscopy is a convenient tool for magnetic study of paramagnetic compounds in solution. The procedure is based on Evans method [1], which involved a 60 MHz NMR spectrometer constant, equal to 2522 x 10^{-4} $Mol^{-1/2}K^{-1/2}$ $mL^{-1/2}Hz^{-1/2}$. The main objective of this work was to determine the magnetic moment of solutions of known 3d-metal based substances as well as of 4f-metal nitrates and of new complexes based on lanthanides.

For this purpose, we used standard NMR tubes with internal coaxial capillaries containing the analyzed sample dissolved in D_2O in the presence of a reference compound, which was $(CH_3)_3COH$) in our study. In order to determine the 400 MHz NMR spectrometer constant, solutions of copper(II) sulfate and nickel(II) chloride, with well known effective magnetic moments, have been used in the experiments. This constant was used afterwards in the measurements and calculations of magnetic moments of nitrates $Ln(NO_3)_3 \cdot nH_2O$ and coordination compounds of lanthanides with general formula $LnBi(edta)(NCS)_2 \cdot 7H_2O$ (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Dz, Ho, Er; n = 5, 7).

The results demonstrated that the experimentally obtained values of magnetic moments of the solutions of complexes correlate quite well with the corresponding calculated values and are close to the values of μ_{ef} obtained for the respective lanthanide nitrate.

Table. Experimental magnetic moments of lanthanide complexes and nitrates versus theoretically calculated and reported values

Ln(III)	μ_{ef} , M.B.			
	Complex	Nitrate	Calculated	Literature
Ce	1.67	2.01	2.54	2.3 - 2.5
Pr	3.11	3.09	3.58	3.4 - 3.6
Nd	3.13	3.18	3.62	3.5 - 3.6
Sm	1.30	1.44	1,23	1.4 - 1.7
Eu	3.13	3.20	3.40	3.3 - 3.5
Gd	6.47	6.93	7.94	7.9 - 8.0
Dy	9.21	9.39	10.65	10.4 - 10.6
Ho	9.26	9.36	10.60	10.4 - 10.7
Er	8.76	9.72	9.58	9.4 - 9.6

The conclusion is that, in solution, the coordination compounds are completely dissociated into aquated lanthanide cations, NCS^- and complex $[Bi(edta)]^-$ anions. The advantage of this method is that it makes possible the determination of magnetic properties involving small amounts (0.1 – 0.2 mg) of compounds in solutions. Moreover, the method permits to establish the exact concentration of paramagnetic metallic species. In this line, the possibility of detecting very small amounts of Ho(III) (0,02 mg/mL or $1 \cdot 10^{-7}$ mol/mL), by means of NMR spectroscopy, has been demonstrated.

References

[1] Evans D.F. J.Cem.Soc., 1959, p.2005.

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