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Thermodynamics and Kinetics of Adduct Formation in Solutions of Bis(N-diisopropoxyphosphinoylthiobenzamido)-copper(II). An ESR Study and Description in Terms of the Donor-Acceptor Model

Kon'kin A., Shtyrlin V., Aganov A., Zabirov N., Garipov R., Zakharov A.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

The equilibrium constants Kad, enthalpies, and entropies of adduct formation, rate constants for adduct formation (kf) and dissociation (kd), and enthalpies and entropies of activation have been calculated for solutions of bis(N-diisopropoxyphosphinoylthiobenzamido)copper(II) (CuL2) in toluene with addition of donor solvents Y (methanol, N,N-dimethylformamide, dimethyl sulfoxide, pyridine, piperidine, diethylamine) over a wide temperature range. The quantities logKad, logkf, and logkd have been found to linearly vary with the donor numbers of the solvents Y; on this basis, an associative character of activation in the formation and dissociation of adducts with copper(II) bischelates has been established for the first time. The constants Kad for CuL2Y are higher than those for other analogous adducts presumably due to the larger fraction of the isomer CuL2Yeq with equatorial coordination of the solvent.