Strange Behaviour of the Methyl Diphenyl Phosphate–$Cu(NO_3)_2$ Complex

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Methyl diphenyl phosphate (MDPP) was used in our laboratory for extraction of acids [1, 2] and nitrates of uranium, thorium, zinc and copper [3, 4]. The striking property of MDPP is its ability to form solid complexes with inorganic salts [5].

Extraction-equilibrium in the copper nitrate–water–undiluted MDPP system is consistent with formation of partially dissociated $Cu(NO_3)_2(H_2O)_3(MDPP)_3$ complex with the equilibrium constant $\sim 4 \cdot 10^{-6}$ in molal units [3]. Considering the optical properties of extraction systems, it was observed that only in the case of $Cu(NO_3)_2$ exists, unusually, time dependent optical activity of the organic phase. There is no absorption in u.v. region when freshly prepared (equilibration of 0.1 N $Cu(NO_3)_2$ with undiluted MDPP, after separating the concentration of copper is about 6 mg $Cu(NO_3)_2$/l of MDPP), highly diluted with benzene and the organic phase measured against benzene. Methyl diphenyl phosphate itself has benzoid absorption band at 220–270 mm [6]. However, when the organic phase is exposed to the day-light for a period of ~24 hrs., or when the sample remains for 10–15 min. in spectrophotometer, suddenly a very strong ($\epsilon \sim 10^5$), broad absorption band with maximum at 305 mm appears and irregular decay of it is observed. Sometimes, repeated irradiations of the sample during the decay period influence significantly the decay-curve, however in any case, the life-time of intermediate species responsible for the reported behaviour does not exceed 2–3 days. It is worth to note, that the organic phase is optically inactive when copper nitrate is replaced by copper sulphate or chloride and the role of oxygen (irradiation with and without the gas) is uncertain. In this stage of investigation, the formation of relatively long-lived Cu(III) complex is postulated, based on some similarity with the copper(III)-peptide complex reported by Margerum *et al.* [7].

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On the Eigenvectors of the g and A Tensors of Copper(II) Substituted in Sites of Low Symmetry

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When a paramagnetic ion is located in a low symmetry environment, the principal directions of the g and hyperfine tensors are by no means trivial. This situation occurs when a diamagnetic complex is doped with paramagnetic ions, particularly in the case of non isomorphism: the substitution will almost certainly induce some distortions of unknown magnitude. Obviously in these cases, it is important to reproduce by calculation not only the eigenvalues but also the eigenvectors. For this purpose, a computer program, recently written by A. Bencini and D. Gatteschi [1] is applied in the case of three copper(II) ESR studies (Cu(II) in bis(β-alanine) zinc(II) nitrate tetrahydrate [2], in cadmium(II) [3] and strontium(II) salicylate [4]. In the references [2–4] the g (or A) values were simply calculated along the *experimental* eigenvectors, assuming an idealized environmental symmetry. In the present note, the usefulness of *calculated* eigenvecors is stressed. Their knowledge may provide a supplementary case in favor of the substitution, as well as some appreciation of the magnitude of the distortion.

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