

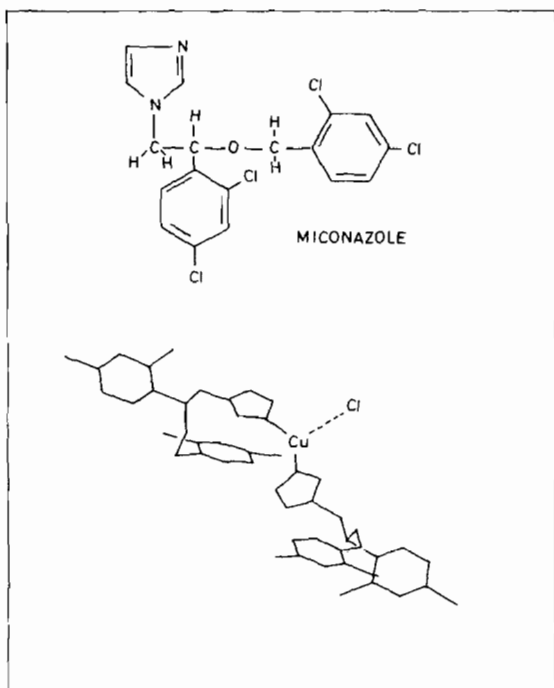
EPR Study of *Trans*-Tetra(miconazole) Copper(II) Chloride Dihydrate $\{(C_{18}H_{14}Cl_4N_2O)_4 \cdot CuCl_2 \cdot 2H_2O\}$

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In this note, we present the results of EPR and optical studies on the title compound. The EPR spectra are recorded from pure (non diluted) single crystals. The coalescence to a single line of the hyperfine structure is not observed here, the distance between the Cu^{++} ions being great enough to reduce the exchange phenomenon.

Recent crystallographic study [1] reveals that the copper ion is six-coordinated to four nitrogen and two chloride atoms in a fairly regular octahedron. The number of molecules per unit cell is only one, making this compound specially suitable for an optical study with polarized light. The experimental results ($g_{\parallel} = 2.27$, $g_{\perp} = 2.05$, $A_{\parallel} = 175$ gauss) will be understood within the framework of an AOM model.



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Solvent Effects on the Spectroscopic Properties of Bis(8-hydroxyquinolino)platinum(II)

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Electronic Spectra

The electronic absorption spectrum of bis(8-hydroxyquinolino)platinum(II), denoted *I*, is strongly dependent on solvent. The low-energy band (A) appears at 22026 cm^{-1} in MeOH and red-shifts in solvents of lower polarity, appearing at 20812 cm^{-1} in the least polar 1,4-dioxan. Similar effects were observed for the high-energy band (B) (λ max 29542 cm^{-1} in MeOH) but in this case the shifts were smaller. A plot of E_T values for the solvents [1] versus ν_{max} for bands A and B showed two distinct linear regions, one referring to hydroxylic solvents and one to non-hydroxylic solvents: the distinction between the two regions was especially marked for band B.

The solvent-dependence of bands A and B shows the same direction and, for band A, the same energy as the shifts observed for the metal-to-ligand charge transfer bands in a number of transition metal complexes [1, 2]. This suggests that band A of *I* complex is also due to an MLCT transition.

Luminescence properties

The luminescence spectrum of *I* consists of a band at 15200 cm^{-1} : over the solvent range EtOH to DMSO, the peak shifts by only 230 cm^{-1} , which is in keeping with its assignment to a spin-forbidden d-d transition as is its energy [3]. The luminescence lifetime of *I* is relatively independent of the solvent (Table I), most values falling within a range of a factor of 2.

TABLE I. Luminescence Lifetime of Bis(8-hydroxyquinolino)platinum(II)

Solvent	$\tau(\mu\text{s})$ 296 K	Isotope Effect
DMSO	2.9 ± 0.3	$\frac{\tau_{CD_3OD}}{\tau_{CH_3OH}} = 1.16$
MeOH	3.72 ± 0.1	
EtOH	5.0 ± 0.1	
$(CH_3)_2CO$	2.2 ± 0.05	
CD_3OD	4.3 ± 0.1	

Deuteration of methanol slightly increases τ . The presence of the small solvent isotope effect suggests a small component of CTTS character in the luminescence transition.

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Complex Metal Hexachlorostannates with Organic Molecules with Nitrogen Atoms as Donors

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Using donicity [1–3] as a term to reflect the complexing properties of the substances in CCl_4 as solvent, a great number of metal hexachlorostannates could be obtained with different ligands of lower donicity as that of the water [4–6] and higher one [7].

The present paper contains data regarding the preparation of coordination compounds in CCl_4 as solvent, with SnCl_4 as chlorine acceptor in Li, Na, K, Rb and Cs as alkalichlorides whose cation has been put to react with organic compounds containing nitrogen donor atom, functioning as ligands that have complexed the metal cation. The general formula of the coordination compounds in solutions is $(\text{ML})_2\text{-SnCl}_6$, where the ligand L could be trimethyl-amine, dimethyl-amine, n-butyl-amine, ethylene-diamine, tetramethylethylene-diamine, pyridine, 2-methyl-pyridine and quinoline.

As the reactions are strongly exothermic they have been carried out in 1M-solutions in CCl_4 referring to each reactant: SnCl_4 and the ligand L. The alkali chlorides have been added to the solution of SnCl_4 in CCl_4 after the solution of SnCl_4 in CCl_4 , added slowly, had led to an abundant formation of stable complex precipitates, which have been filtered and washed with CCl_4 .

It is interesting to note that an attempt to obtain complexes using CuCl showed that no analogous complexation is achieved and the reaction does not yield a unitary product, while a darkening of the solution to dark blue has been observed, explained through the formation of Cu(II) aminocomplexes.

Acknowledgement

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Structural-Energetical Aspects of Interreaction in Carbonyl Metal Systems

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Theoretical arguments have so far been based on the earlier unknown facts of the possibility of the tensimetric method with the membrane zero-manometer for the definition of the solubility and thermodynamic properties of the dissolution process. In this report the structures of metal carbonyls are compared with the thermodynamic characteristics of the dissolution process of the same compounds and clusters form of the group elements. The alternation of the characteristic frequencies of M–C and C–O bonds of iron carbonyls gives the possibility to consider that the negative end of dipole moment, the order bond and the dissociation energy of metal carbonyl bond (DM –CO) do not increase practically