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Adducts of Some Divalent Metal (Zn^{II}, Cd^{II}, Hg^{II}, Sn^{II}) Chlorides with Biologically Important Ligands such as 1-Aminoanthraquinone

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The considerable chemical and biological interest in anthraquinones and their substituted derivatives has been aroused by their wide field of application, such as in electrochemistry, analytical chemistry and physical chemistry [1, 2] as well as biochemistry. In this last field recent advances in anthracycline studies are stimulating the design of new compounds and new therapeutic regimens [3]. Their antitumor activity has been suggested to be related to the planar configuration structure intercalating into DNA and RNA molecules, so that they act as synthesis inhibitors [4].

Since the interactions with metal ions seem to play an important role in the explanation of most of their chemical and biological activites, in this paper we report an investigation into the coordinating ability of 1-aminoanthraquinone toward divalent metal ions such as Zn^{II}, Cd^{II}, Hg^{II} and Sn^{II}.

Experimental

Preparation of the Adducts

All the red compounds were obtained by mixing ethanolic solutions of metal halide and the ligand in 3:1 to 1:3 ratios.

$ZnCl_2L_2$: *Anal.* Calcd. for $C_{28}H_{18}N_2O_4ZnCl_2$: C, 57.65; H, 3.09; N, 4.80. Found: C, 57.14; H, 3.12; N, 4.94. $Cd_2Cl_4L{\cdot}2H_2O$: *Anal.* Calcd. for $C_{14}H_{13}NO_4Cd_2Cl_4$: C, 26.84; H, 2.07; N, 2.23. Found: C, 26.83; H, 1.97; N, 2.42. $HgCl_2L_2$: *Anal.* Calcd. for $C_{28}H_{18}N_2O_4HgCl_2$: C, 46.79; H, 2.50; N, 3.90. Found: C, 46.67; H, 2.52; N, 3.97. $Sn_2Cl_4L_3{\cdot}2H_2O$: *Anal.* Calcd. for $C_{22}H_{31}N_3O_8Sn_2Cl_4$: C, 46.45; H, 2.85; N, 3.87. Found: C, 46.15; H, 2.81; N, 4.11.

Physical Measurements

IR spectra in nujol mull on KCl pellets as support and in KCl pellets (4000–250 cm^{-1}) and in nujol mull in polythene as support (500–100 cm^{-1}) were recorded on a Perkin Elmer 180 spectrophotometer. The electronic spectra of the solid samples were recorded on a Shimadzu MPS 50L spectrophotometer. Samples were prepared by grinding the compounds on a filter paper as support. Raman spectra were not recorded as the compounds decompose under laser radiation. C, H and N were analysed with a Carlo Erba Elemental Analyser 1106.

Results and Discussion

The more relevant IR bands (Table I) are unambiguously assigned by comparing the spectra of the present complexes with those of the ligand, the hydrochloride salt of the ligand and their deuterated derivatives. For all the complexes the ligand bands appear slightly modified by coordinations – a common feature already observed for a similar class of ligands, benzophenones and their substituted derivatives, previously examined [5].

In the far-IR spectra of the complexes, only for the cadmium(II) and mercury(II) ones can the

TABLE I. More Relevant IR Bands of the Ligand, the Hydrochloride Salt of the Ligand, their Deuterated Analogues and the Compounds.

	L	L (deuter.)	L·HCl	L·DCl	Compounds
$\nu(NH_2)$	3420mw	3425ms	2840vsb[c]		3420mw
	3300w	3310ms	2560s		3300w
$\nu(ND_2)$		2590ms			
		2500w			
		2470s			
$\nu(CO)$[a]	1665s	1667vs	1675vs	1675s	1665s
$\nu(CO)$[b]	1632s	1632vs			1635s
$\delta(NH_2)$	1605vs	1608w	1520vs[d]		1608vs

[a] Referred to the free CO group. [b] Referred to the CO group involved in the intramolecular hydrogen bond with the NH_2 group. [c] $\nu(NH_3^+)$. [d] $\delta(NH_3^+)$.

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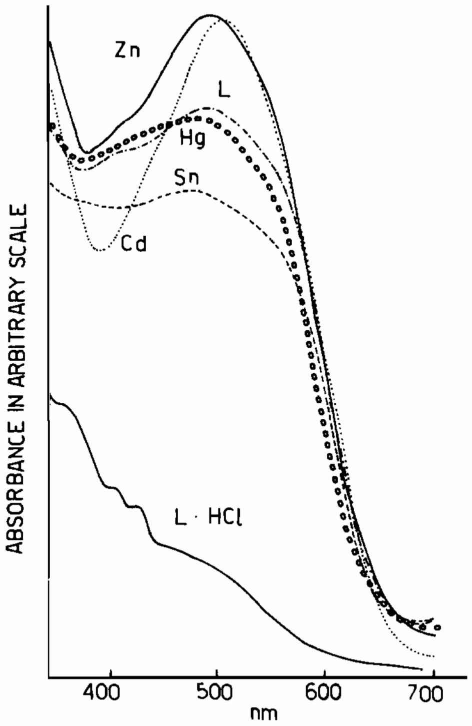

Fig. 1. Charge-transfer bands of the ligand, the hydrochloride salt and the adducts.

metal–chlorine bands be unambiguously assigned. In the cadmium complex the very strong and broad band appearing at 176 cm^{-1} is consistent with the presence of bridging chlorine atoms, while in the mercury complex the strong band at 353 cm^{-1}, in agreement with the literature data [7], strongly suggests the presence of linear $HgCl_2$ units [5].

The electronic spectra in the visible region of the title compounds are characterized by a strong and broad absorption band centered around 500 nm which is assigned to the ligand intramolecular $\pi \rightarrow \pi^*$ charge transfer transition from the amino to the carbonyl groups according to previous authors [6]. Such a band present in the uncoordinated ligand disappears when the ligand is protonated, namely when the nitrogen lone pair is mainly involved in a strong σ bond. This $\pi \rightarrow \pi^*$ transition, still present in the complexes, seems to be connected to weak metal–ligand interactions so that the electronic structure of the filled and virtually molecular orbitals of the ligand is slightly affected by coordination. Moreover, the intraligand N–H···O hydrogen bond can also help to maintain an overall π-electron structure in the ligand itself, as has been demonstrated for the 2-aminobenzophenone–mercury(II) bromide (1:2) adduct, the crystal structure of which has been reported [5] (Fig. 1).

Such evidence leads to the conclusion that the biological activity of 1-aminoanthraquinone, connected with its steric and electronic structure, can be gradually varied *via* coordination to metal ions without losing its peculiar properties.

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