The main features of the EPR spectrum of the purple solution at 77 K are seen in Fig. 1. When the spectrum is measured at a higher temperature (up to 250 K), the symmetry of the paramagnetic species remains unchanged. However at temperatures higher than 170 K, the Rh-hyperfine structure disappears and eventually the spectrum of the Figure (measured at 170 K) is observed.

The EPR spectrum is attributed to a Rh(II) complex, the formation of which is totally reproducible. On the basis of experimental and theoretical results published in the case of EPR spectra of d^7 'low spin' elements, we propose a C_{2v} symmetry for the Rh(II) complex, the unpaired electron being principally located in a $d_{x^2-y^2}$ orbital. This electron is largely delocalized on the only chloride ion of the complex, on the symmetry axis.

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Magnetic Resonance Spectra of Some Homo- and Hetero-Dinuclear Paramagnetic Metal Complexes with 1,5-Diphenyl-pentane-1,3,5-Trione

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The spectroscopic and magnetic properties of heterodinuclear transition metal complexes are a topic of current chemical interest, since they can largely expand the number of experimental data on exchange interactions and give new information to correlate the magnetic properties with the structural features of the complexes.

Magnetic resonance spectroscopy has been shown to provide powerful tools for detecting and investigating such chemical species [1, 2]. In particular PMR can provide information on the role of the ligands on the superexchange pathway as well as on the electronic states of the coupled metal pairs, while ESR can be used to obtain the spin hamiltonian parameters, which help in the interpretation of the PMR experimental data.

We have considered the complexes formed by the tridentate ligand 1,5-diphenyl-pentane-1,3,5-trione. This ligand is known [3] to form dinuclear antiferromagnetically coupled nickel(II) and cobalt(II) complexes of general formula $M_2L_2(py)_4 \cdot 4py$ (py = pyridine). We have also synthesized the manganese(II) and zinc(II) derivatives and solid compounds containing the heterodinuclear complexes. Their ESR and ^1H NMR spectra will be reported and discussed.

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ESR Spectra of Some Adducts of Cobalt(II) Acetylacetonate

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We have recently reported that the pattern of g values in tetragonal octahedral cobalt(II) complexes is dramatically affected by the π-bonding ability of the equatorial and axial ligands [1]. Pursuing our work in this field, we studied several adducts of cobalt(II) acetylacetonate, in order to check how the principal g values and directions are affected by the nature of the axial substituents. The ESR spectra of $Co(acac)_2L_2$ [L = 6-methylquinoline (I); pyridine (II); water (III)] were recorded at 4.2 K and they were interpreted using the method based on the Angular Overlap Model previously developed [2].

Single crystal ESR spectra allowed us to obtain the following g values: $g_1 = 5.67$, $g_2 = 4.11$, $g_3 = 1.90$ for (I); $g_1 = 5.83$, $g_2 = 3.92$, $g_3 = 1.98$ for (II); $g_1 = 6.84$, $g_2 = 2.74$, $g_3 = 1.88$ for (III). The g_3 direction is close ($\simeq 20°$) to the Co–axial ligand bond direction. For (III) also the spectra of the complex diluted in a Mg lattice were recorded. The spectra showed g values equal to those of the undiluted derivative and a hyperfine structure complicated by second order effects and quadrupolar or nuclear Zeeman interactions. The A values, obtained through a minimization method which accounts for second order effects are: $A_1 = 180 \times 10^{-4}$ cm^{-1}, $A_2 = 20 \times 10^{-4}$ cm^{-1}, $A_3 = 39 \times 10^{-4}$ cm^{-1}, the A tensor being colinear, within 2°, with the g one.

The ESR data for the complexes show completely anisotropic g values, with the rhombicity, $g_1 - g_2$, increasing on passing from quinoline to water adducts. Further the projection of the g_1 and g_2 directions in the CoO_4 plane are coincident with the projections of the Co–O bond directions in the same plane for (I) while they are rotated by $\simeq 20°$ for (III). As the structural features of chromophores are quite similar for (I) and (III), the principal cause of these differences must be the different nature of the metal–axial ligand interactions for 6-methylquinoline and water.

The simple assumption of an increase of π-bonding ability, as expected passing from nitrogen bases to water and of the anisotropy of this interaction, based on structural considerations, allowed us to calculate the g and A tensors in a good agreement with the experimental findings. Although the fits we found are not unique, it is important that the experimental data can be reproduced using the minimum number of parameters and varying their values according to the expectations on the chemical behavior of the ligands.

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Interactions between Sodium Dithiocarbamates and p- and d-Block Metals

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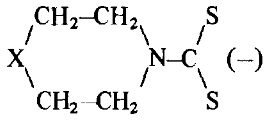
Working on the problem of the interactions between p- and d-block metals and dithiocarbamate sodium salts as ligands, we report in this study the derivatives of Cr(III), Mn(III), Pb(II), Sn(II), Os(II) and Os(III) with



X = CH_2 Pipdtc
= O Morphdtc
= N–CH_3 CH_3–Pzdtc
= S Timdtc

We have previously described the complexes of many transition metals with the above dithiocarbamates, derivatives of iridium phosphine and arsine hydrides, and monohalobisdithiocarbamate iron(III), antimony(III) and bismuth(III) derivatives [1].

This paper is an extension of the previously reported studies on the dithiocarbamates in which dialkyl groups are replaced by heterocycles. It is of interest to study the influence of the different heterocyclic groups on the C$\overset{..}{-}$N and C$\overset{..}{-}$S bands and, consequently, on the electronic structure of the complexes. The nature of the heterocycle is important in the behaviour of the dithiocarbamates as ligands owing to the variation in the electron releasing ability of the different amines. The compounds are microcrystalline, soluble in N,N'-dimethylformamide (DMF) and non-conducting in this solvent.

Our manganese(III) derivatives have a μ value in the 4.8–4.9 B.M. range and these values are typical of high-spin complexes. These trisdithiocarbamates can be readily prepared by aerial oxidation of the suspension produced when aqueous or aqueous–ethanolic solutions are mixed. However a recrystallization under nitrogen is necessary to prevent aerial decomposition.

The thioureide band near 1500 cm^{-1} indicates considerable double bond character in C$\overset{..}{-}$N bond. This fact could be ascribed to the electron releasing ability of the heterocyclic group, which forces high electron density towards the sulphur atoms, *via* the π system, thus producing greater double-bond character in the carbon–nitrogen bond, and shifting ν(C$\overset{..}{-}$N) to higher energies. The band attributed to the prevailing contribution of ν(C$\overset{..}{-}$S) is indicative of a bidentate behaviour of the dithioligands and this fact is confirmed by the blue shift of the ν(C$\overset{..}{-}$N) mode.

The ν(C$\overset{..}{-}$N) band undergoes a blue shift greater in the chromium(III), manganese(III), osmium(III) and osmium(II) derivatives than in the tin(II) and lead(II) complexes. This behaviour could be explained by considering either the different stereochemistries of the complexes or the fact that the three first metals are of the d-block, while the last two belong to the p-block. Perhaps because of the rigid heterocyclic ring system, which shows less tendency to release electrons to the carbon–nitrogen bond, this bond has a less double-bond character; this tendency to release electrons is less in the p-block metal derivatives than in the d-block ones.

The electronic spectra have been studied and will be discussed in detail. The room temperature magnetic moment values for Cr(III), Mn(III) and Os(III) derivatives are in agreement with the literature data; all the remaining complexes of Pb(II), Sn(II) and Os(II) are diamagnetic.