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Dithiocarbamate Complexes of Rhodium(III), Iridium(III), Palladium(II) and Platinum(II)*

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Abstract

We report the preparation and characterization of the complexes of rhodium(III), iridium(III), palladium(II) and platinum(II) with the following ligands: Pzdtc, N-MePzdtc, N-PhPzdtc, Pipdtc, 4-PhPipdtc, Morphdtc, Timdtc, and with their methyl esters.

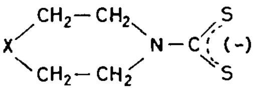
The dithio ligands act as bidentate *S*,*S'*-donors in all the new derivatives. From the electronic absorption spectra the values of the ligand field parameters were determined. The nephelauxetic parameters are indicative of a strong covalency in the metal–ligand bond. All the compounds reported here are diamagnetic.

Introduction

Action of sodium diethyldithiocarbamate (DDTC) against cisplatin (*cis*-dichlorodiammineplatinum(II)) nephrotoxicity has been tested in *in vitro* and *in vivo* experiments [1, 2]. This chelating molecule, appropriately administered, inhibits cisplatin toxicity and increases the efficacy of this drug.

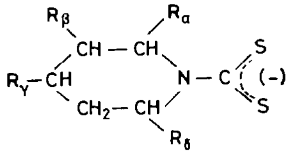
Results and Discussion

We report the preparation and characterization of the complexes of rhodium(III), iridium(III), palladium(II) and platinum(II) with the following dithiocarbamate sodium salts as ligands:



X = NH (Pzdtc), N-CH_3 (N-MePzdtc), N-C_6H_5 (N-PhPzdtc), CH_2 (Pipdtc), C_6H_5-CH (4-PhPipdtc), O (Morphdtc), S (Timdtc)

and with the methyl derivatives of piperidinedithiocarbamate, having a CH_3 group in 2-, 3-, 4- and 2,6-positions of the heterocyclic ring:

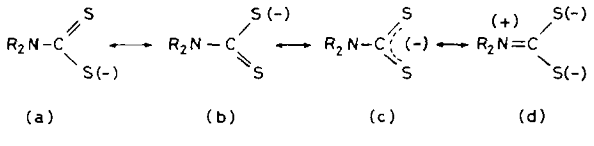


R_α	R_β	R_γ	R_δ	
Me	H	H	H	2-CH_3-Pipdtc
H	Me	H	H	3-CH_3-Pipdtc
H	H	Me	H	4-CH_3-Pipdtc
Me	H	H	Me	2,6-CH_3-Pipdtc

As an extension of our study we are examining the methyl esters and the thiouramdisulfides of the above dithiocarbamates with the same metals. Our intent is to clarify the synergistic effect of the dithiocarbamates by carrying out detailed studies of the above reported series of ligands, taking into account that even the smallest variations in the chemical properties of the compounds are related and reflected in variations of pharmacobiological properties of these products as drugs.

The band attributed to the prevailing contribution of the $\nu(C \overset{...}{=} N)$ is found in the ligands between the stretching frequencies of $\nu(C{=}N)$, 1690–1640 cm^{-1}, and $\nu(C{-}N)$, 1350–1250 cm^{-1}; this fact indicates considerable double-bond character in the carbon–nitrogen bond. This band undergoes a blue shift on passing from the free ligands to the complexes for the three series of ligands.

The $\nu(C \overset{...}{=} N)$ stretching mode of the heterocyclic dithiocarbamates is at lower wave numbers than the $\nu(C \overset{...}{=} N)$ of the dialkyldithiocarbamates; taking into account the structure of the dithio anions which can be represented by the following equilibrium we can conclude, according to our previous studies, that the contribution of the structure (d), greatest for the dialkyl complexes and lower for more complex aliphatic chains, is relatively small for the heterocyclic derivatives.



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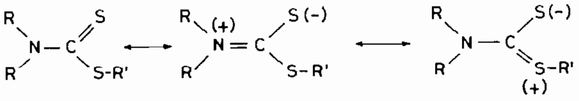
Perhaps owing to the rigid heterocyclic ring system which shows less tendency to release electrons to the carbon–nitrogen bond, this bond has less double-bond character.

As regards the influence of the position of the methyl group on the piperidine ring, the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ value increases in the order:

$2\text{-CH}_3\text{-Pipdtc} < 3\text{-CH}_3\text{-Pipdtc} < 4\text{-CH}_3\text{-Pipdtc}$

Dithiocarbamate ester molecules are resonance hybrids of the canonical formulas:



(a) (b) (c)

When these ligands act as monodentate through the thiocarbonyl system the carbon–nitrogen double bond is enhanced, with a parallel $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ shift to higher frequencies with respect to the corresponding uncoordinated molecule, with a predominant contribution of the form (b).

A blue shift of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ mode is observed in the derivatives of the thiouramdisulfides; the increase in the frequency of this thioamidic band results from the increase in the double-bond character of the carbon–nitrogen bond. Furthermore the position of the band is affected by the nature of the central atom in the complexes and is shifted to lower frequencies as follows: Ir > Rh and Pt > Pd, and this is a reflection of the higher electron-acceptor ability of Ir than Rh, and Pt than Pd.

The band at about 1000 cm^{-1} is attributed to the stretching vibration $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$. This vibrational mode indicates whether the dithiocarbamato moiety is monodentate or bidentate in the $\mathrm{Rdtc}^{(-)}$ derivatives. The presence in our complexes of only one strong band in this region strongly supports bidentate coordination of the dithio ligand, a doublet being expected in the 1000 ± 70 cm^{-1} region for monodentate behavior.

Passing to the dithiocarbamic esters, the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ mode depends on the metal:ligand stoichiometric ratio in the complexes obtained. In fact the spectra of the 1:1 derivatives show two bands, while three bands are present in the spectra of the 1:2 complexes.

In the far infrared region new bands due to $\nu(\mathrm{M{-}S})$ are present in the 280–350 cm^{-1} for the Pd(II) and Pt(II) complexes and between 320–335 cm^{-1} for the Rh(III) and Ir(III) derivatives.

The electronic spectra of the palladium(II) and platinum(II) derivatives are indicative of square-planar geometries, while the derivatives of rhodium(III) and iridium(III) low-spin type ($\mathrm{t}^6{}_{2g}$) have octahedral configurations.

The complexes have been studied by thermal analysis, TG and DTG techniques; the palladium(II) and platinum(II) derivatives were thermally stable up to 400 °C. Above this temperature decomposition sets in and continues, in the case of palladium, giving polysulfides of the type $\mathrm{Pd}_x\mathrm{S}_y$ which slowly give PdO; in the case of platinum, beyond 400 °C a single step decomposition starts and proceeds with the loss of the ligands giving metallic platinum sponge as the end-product. The rhodium(III) derivatives were stable up to 375 °C; beyond this temperature a rapid mass loss up to 500 °C occurs corresponding to the decomposition of the complexes to the metal. The next step over 500 °C corresponds to oxidation of the metallic rhodium to the black $\mathrm{Rh_2O_3}$ oxide. The iridium(III) complexes, stable up to 360 °C, undergo decomposition in the 360–500 °C range, giving metallic iridium as product. From this last temperature up to 830 °C, $\mathrm{Ir_2O_3}$ is obtained.

In addition to the techniques mentioned above, XPS and UPS, multinuclear NMR, and X-ray diffraction studies are in progress.

References

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