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Structure modelling and comparison between the charge-transfer capacities of diphosphinic bidentate ligands in two series of ruthenium(II) complex compounds

Research article

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Abstract
As diphosphinic bidentate ligands are usually strong σ donors, this work presents a comparison between the charge-transfer capacities of two such ligands namely 1,2-bis(diphenylphosphino)ethane (denoted as BDPPE) and *cis*-1,2-bis(diphenylphosphino)ethene (refered to as CBDPPE).

Their π-acceptor capacity, influenced by the presence of a π-acceptor molecule, is determined by the quantum-mechanical properties of phosphorus *d* orbitals. Therefore, a quantum-mechanical study on the charge-transfer capacities of these two diphosphinic ligands has been carried out in two series of ruthenium complex compounds. Hartree-Fock method and the HyperChem 8.0.10 software were used.

Keywords: ruthenium(II) complex compounds, diphosphinic bidentate ligands, charge-transfer capacity, Hartree-Fock method, HyperChem 8.0.10

1. INTRODUCTION

Ruthenium polypyridine complexes have been lately investigated as chromophor centers of supramolecular compounds, in order to create systems capable of transforming light energy to chemical bond energy. Recently, ruthenium(II) polypyridine-phosphinic mixed-ligand complexes have arose considerable interest [1,2].

These complexes feature increased photochemical stability and they represent real building-blocks for new photo-stable supramolecular systems. Introducing diphosphinic bidentate ligands into the inner coordination sphere of ruthenium(II) polypyridine complexes affects their properties: the oxidation potential strongly increases, the luminescence decay times and quantum yields also increase, whereas the absorption band in the electronic absorption spectrum, which is related to the charge transfer from Ru(II) d_π atomic orbitals (AO's) to π-antibonding molecular orbitals (MO's) of the polypyridine ligand, shifts towards violet [2].

In order to find a relationship between the measured characteristics and also to explain and schematize available evidence, it is suitable to relate experimental findings to the electronic structure of these complexes, so quantum-mechanical calculations must be performed to explain the nature of the metal-ligand bond and the mutual effect of the ligands in polypyridine-diphosphinic complexes.

The nature of the bonds between the phosphorus-containing ligands and the transition metal, as well as both the relative σ and π contributions, the involvement of phosphorus *d* orbitals as acceptors of the electron density transferred from metal *d* AO's are still subjects of discussion in different researches [2, 3].

The hypothesis that phosphorus *d* AO's are involved in phosphorus-metal bonding is commonly accepted in coordination chemistry, but recent quantum-chemical calculations have released any doubt on its validity [1].

Even if calculations predict appreciable involvement of phosphorus *d* orbitals, it is still hard to tell whether the *d* AO's have the only function of polarizing phosphorus *p* AO's or they are really involved into to the valence shell and thus into bond formation.

Knowledge of the nature of the metal-phosphorus bond is of primary importance for understanding electronic interactions in the inner coordination sphere of polypyridine-diphosphine mixed-ligand complexes [4].

As a rule, π-acceptor properties of ligands (such as NO^+, CO, pyridine, 2,2`-dipyridine) are associated with the presence of low-lying π-antibonding unoccupied orbitals.

When a complex contains several such ligands in its inner sphere, they compete for metal d_{π} electrons, which affects $d_{\pi} \rightarrow \pi^*(L)$ excitation energies.

Phosphinic ligands have no low-lying π^* MO's (sterically localized in the vicinity of the metal-ligand bond [2], so the electronic absorption spectra of phosphine complexes consequently display no $d_{\pi} \rightarrow \pi^*(L)$ bands in the low-energy region).

If, however, there are some grounds to regard phosphines as electron acceptors, this is a particular class of acceptor ligands which deserves special further attention.

2. THE TWO SERIES OF Ru(II) COMPLEX COMPOUNDS

In the present work the contribution of phosphorus *d* AO's into valence interactions was evaluated by investigating the effect of the phosphorus-containing ligand on the electronic structure of the rest complex.

Also, its effect on the population of metal d_{π} AO's, on the π-acceptor ability of the other ligands, as well as on the metal-ligand bond multiplicity were studied.

As it was previously stated, this paper presents a comparison between the charge-transfer capacities of two diphosphinic bidentate ligands.

The first one was 1,2-bis(diphenylphosphino)ethane (BDPPE) and the second one was *cis*-1,2-bis(diphenylphosphino)ethene (CBDPPE).

Usual ligands: ammonia, 2,2`-dipyridine (dipy) and ethylenediamine (en) were also used for this comparison.

The study has been developed in two series of ruthenium complex compounds:

- series 1, $[Ru(AA)(NH_3)_4]^{2+}$
  (where (AA) = dipy / BDPPE / CBDPPE)
- series 2, $[Ru(AA)(dipy)_2]^{2+}$
  (where (AA) = en / BDPPE / CBDPPE).

The first series aims to compare the donor-acceptor capacities of the (AA) ligands in the absence in the inner sphere of other π-ligands, whereas the second one aims to evaluate the effect of ligands (AA) on the π-acceptor capacity of 2,2`-dipyridine.

Calculations were computationaly performed using the nonempirical Hartree-Fock method, that was augmented with the polarization function of the phosphorus atom.

All these complexes were also modelled with HyperChem 8.0.10 (trial version) software application, as shown in figures 1a-c for the first series of Ru(II) complex compounds and in figures 2a-c for the second series.

In these figures, the hydrogen atoms have not been shown [5].

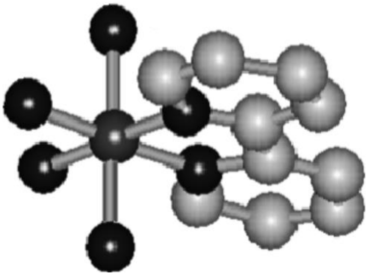

Figure 1a. $[Ru(dipy)(NH_3)_4]^{2+}$

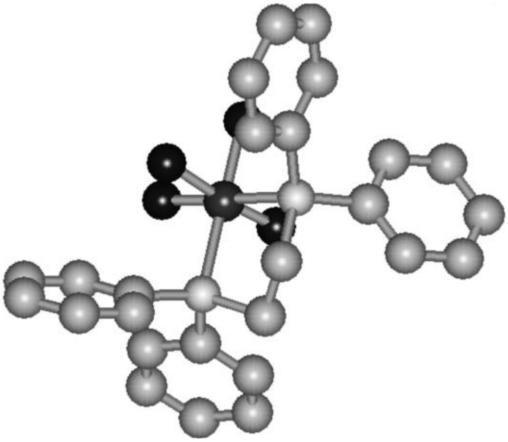

Figure 1b. [Ru(BDPPE)$(NH_3)_4$]$^{2+}$

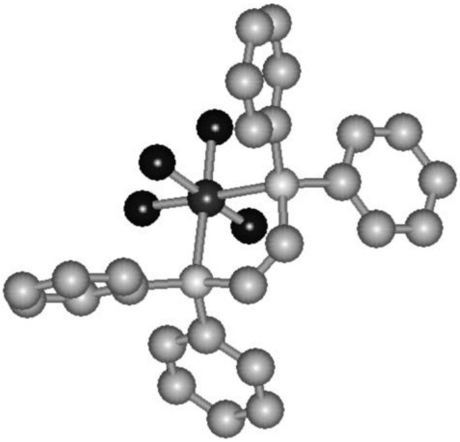

Figure 1c. [Ru(CBDPPE)$(NH_3)_4$]$^{2+}$

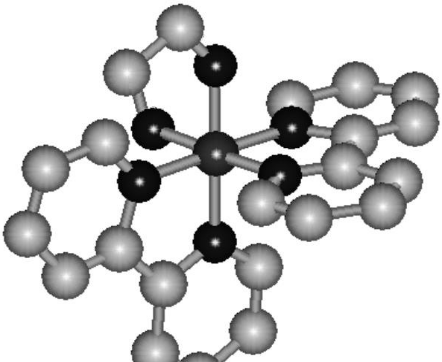

Figure 2a. [Ru(en)$(dipy)_2$]$^{2+}$

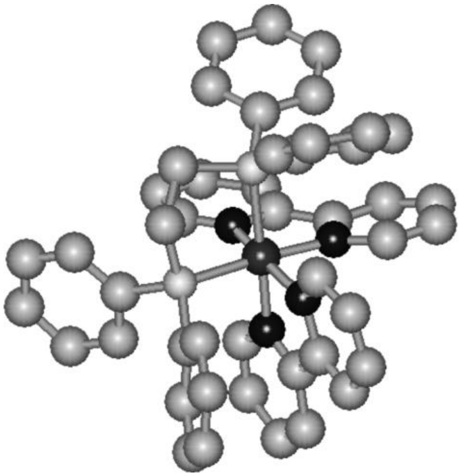

Figure 2b. [Ru(BDPPE)(dipy)$_2$]$^{2+}$

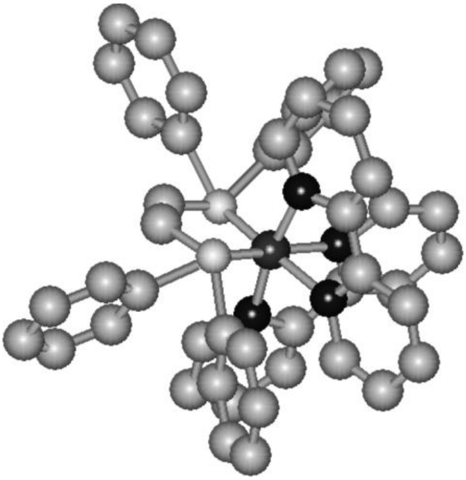

Figure 2c. [Ru(CBDPPE)(dipy)$_2$]$^{2+}$

3. QUANTUM-MECHANICAL STUDY

Figures 3a-c show the diagrams of higher occupied MO's for compounds in series 2.

The highest occupied molecular orbitals (HOMO's) of the diphosphine complexes are mostly phenyl *p* orbitals, with small contributions of π orbitals of the other fragments. Next follows (about 1eV lower) the π MO of dipy and then (0.2-0.4 eV lower than that) three MO's with more than 50 % contributions of ruthenium *d* AO's.

In the complex shown in figure 2c, the Fe *d* orbitals are followed by a MO to which mostly contribute the *p* orbitals of the C_2H_2 group in diphosphine; both complex compounds have (in the same region) a mixed orbital to which almost equally contribute the *p* orbitals of all fragments.

The comparison between the three members of serie 2 shows that the diagram of higher occupied MO's of the diphosphine complexes can roughly be represented as a superposition of MO's of the $[Ru(dipy)_2]^{2+}$ fragment and of diphosphine ligands.

In particular, the HOMO of complex shown in figure 2a (as dipy π MO lies at cca. -12 eV) remains no longer HOMO in the diphosphine complexes, but it preserves its energy.

The lowest unoccupied molecular orbitals (LUMO's) of the diphosphine complexes are almost pure dipy π^* MO's, phosphorus *d* orbitals being situated much higher on the energetic diagram.

According to the commonly accepted assignment, the band in the visible absorption spectrum of bipiridyl-diphosphine complexes is caused by a $d \rightarrow \pi^*$(dipy) charge transfer, like in the other Ru(II) bipyridine complex compounds [1, 2].

The energy gap between MO's is mostly due to Ru(II) d_{π} AO's, whereas the LUMO's energies of complexes in series 2 seems to be almost the same.

This fact suggests that, most probably, the explanation for the experimentally observed shifts of the bands in the spectra of the diphosphine complexes compared with other dipyridine complex compounds should be attributed to the solvation effect.

By taking solvation into account, the energies of MO's mostly represented by Ru(II) *d* orbitals increases by ~ 0.5 eV, whereas the energy of phenyl higher occupied MO's slightly decreases (as it can be seen in Figures 3d and 3e). The energy gap between HOMO and Ru(II) *d* orbitals decreases from 2.1 to 1.3 eV, but phenyl MO's still remain highest occupied MO's of the complex.

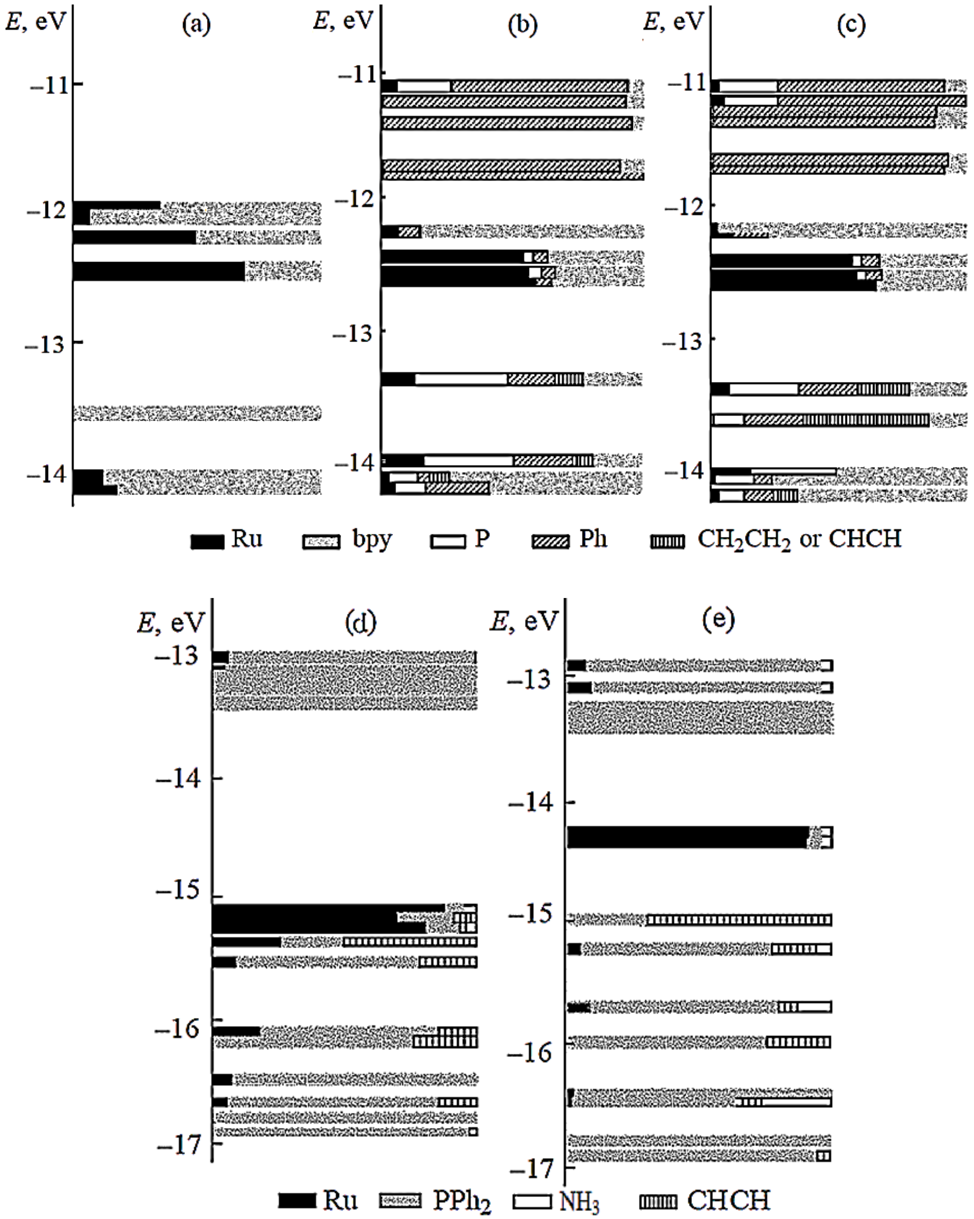

Figure 3. HOMO's diagrams
a-c: comparison within 2, *i.e.*, [Ru(AA)(dipy)$_2$]$^{2+}$,
where AA = en (a) / BDPPE (b) / CBDPPE (c);
d, e: isolated and respectively solvated complex [Ru (CBDPPE)(NH$_3$)$_4$]$^{2+}$ – the last in series 1

4. CONCLUSIONS

Quantum-mechanical study on the charges on Ru(II) and ligands in the complexes shows that BDPPE and CBDPPE are proved to be stronger σ donors than ethylenediamine.

By including solvation as well into study, the difference in charge transfer between the complexes with different bidetante ligands (AA) gets smaller, but the values obtained for CBDPPE are still much larger than for the other ligands (dipy becomes a weaker donor than NH_3).

As it might be seen, coordination to ruthenium(II) renders the ligands less polarized (Ph and C_2H_2 groups are depleted of electron density, as the negative charge on these ligands decreases); at contrary, phosphorus accepts electron density (it gets less positive, showing that the phosphorus *d* AO's are really involved in chemical bonding).

This analysis showed that diphosphine ligands, when incorporated in ruthenium(II) bipyridine-diphosphine mixed-ligand complexes, behave mostly as σ-donors.

Particularly, the ligands taken into our study (BDPPE and CBDPPE) are comparable in π-acceptor capacity, which obviously concerns the phosphorus d_{π} orbitals.

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Thermodynamic study of the vapor-liquid equilibrium (VLE) data for the binary system butyric acid–water

Research article

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Abstract
The paper presents the thermodynamic analysis of the Vapor-Liquid Equilibrium (VLE) data, for the system butyric acid-water. The binary data were obtained at atmospheric pressure in a recirculatory still, designed by Gothard. To ensure a proper mixing of the components in the liquid phase, the equilibrium cell is provided with a magnetic stirrer. The experimental VLE data were checked for thermodynamic consistency using a procedure, consisting in numerical integration of the coexistence equation of the equilibrium phases. A correction term for the non-ideality of the vapour phase was considered by using the Hayden O'Connell correlation to estimate the second virial coefficients, B_{ii} and B_{jj}.

Keywords: *thermodynamic consistency, virial cooficients, butyric acid*

1. INTRODUCTION

It is well known that the efficiency of multicomponents systems distillation depends of the experimental procedures to obtain binary VLE data sets. The thermodynamic analysis of the equilibrium data and adequate correlation models are necessary to calculate the design parameters of the distillation equipment.

Besides the purity of the components, the quality of the experimental VLE data, depends on the experimental equipment and techniques used to obtain the binary data sets. In general, the results of VLE data measurements are affected by errors, from the experimental measurements of the equilibrium parameters, namely, the boiling temperature of binary mixtures, the working pressure and the compositions (mole fractions) in both, liquid and vapor phases (x, y).

An inadequate design and operation of the experimental setup, used for obtaining VLE data, are the major sources of the systematic errors, caused by not reaching the equilibrium status between the phases in contact. Thermodynamic consistency tests, verifying the experimental VLE data, are used to identify these types of errors.

Several works present VLE data of mixtures containing butyric acid in binary and ternary systems with water and butanol but mostly, the data are presented without the thermodynamic consistency analysis or, if performed, the methods are empiric and neglect the non ideal behavior of the vapour phase.

The paper reports the results of the thermodynamic consistency analysis of the experimental VLE data, for the system butyric acid – water using a model – free procedure [1].