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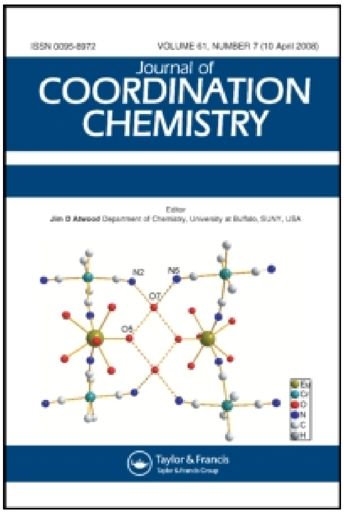

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ELECTRONIC EFFECTS OF DONOR AND ACCEPTOR SUBSTITUENTS ON DIPYRIDO(3,2-a:2',3'-c)PHENAZINE (dppz)

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The chelate ligands 11-R-dipyrido[3,2-a:2′,3′-c]phenazine, **dppz-R** (R = NH_2, CH_3, H, COOH, NO_2) and the Re(dppz-R)$(CO)_3$Cl (R = NH_2, COOH, NO_2) complexes were synthesized and characterized by conventional techniques. The influence of the donor and acceptor properties of the R substituents on the ligand properties were studied by spectroscopic techniques such as ^{1}H-NMR and UV-Vis. Theoretical calculations were also achieved, mainly to interpret and understand the experimental spectra.

Keywords: Electron effects; Theory; Donor substituents; Acceptor substituents; Ligand properties

INTRODUCTION

Dipyrido[3,2-a:2′,3′-c]phenazine (**dppz**) complexes have been reported in different contexts [1], as in DNA intercalation studies [1c, 1e] or as potential solar cell dyes [1f]. The dppz ligand combines interesting properties, as its rigid and planar highly conjugated aromatic structure,

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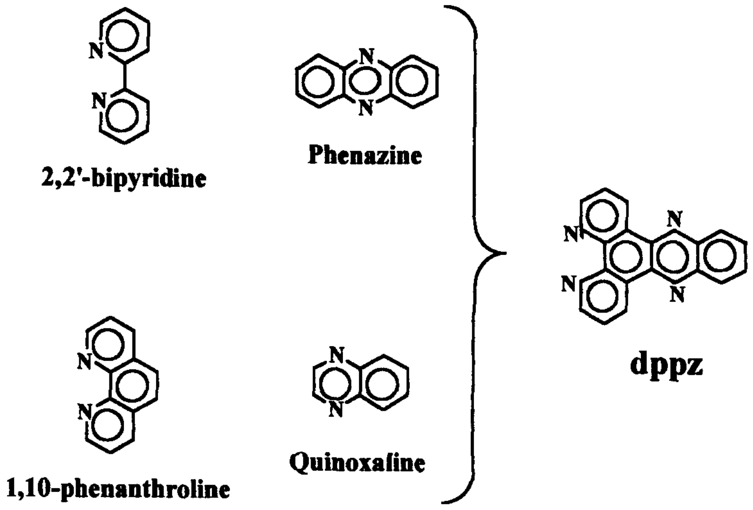
as well as its bidentate coordination capacity. The structure of dppz has been interpreted as originating from the "condensation" of 2,2′-bipyridine and phenazine, or as a "condensation" of quinoxaline and 1,10-phenanthroline [1a].



Substitution on the phenazine fragment can produce a variation in the ligand donor or acceptor properties, modifying its coordination capacity as a transition metal cation Lewis acid. In this paper, the effect of different substituents on the dppz donor capacity was studied by ^{1}H-NMR, UV-Vis, and cyclic voltammetry. Theoretical calculations correlated well with experimental data and were helpful in understanding the behavior. Re complexes with the ligands are also reported.

EXPERIMENTAL

Physical Measurements

UV-VIS spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AC/200, 200 MHz spectrometer with TMS as reference. IR spectra were recorded as KBr pellets in a Bruker Vector 22 FTIR spectrometer. Cyclic voltammetry was performed with Bas CV-5OW 2.3 MF-9093 equipment.

Theoretical Calculations

The electrostatic charges on the different atoms were calculated for the optimized ligand geometries by means of the PM3 Spartan parameterization package [2a]. For electronic spectra, the optimized Spartan program geometries were used as input geometries in the Hyperchem program [2b]. The electronic spectrum of the complex was calculated at the ZINDO/S level using a Restricted Hartree-Fock method (RHF) with configuration interaction (CI). A total of 25 occupied and 25 unoccupied orbitals were used in the CI calculation.

Materials

All chemicals were reagent grade and used as received. 1,10-phenanthroline, 2,3-diaminonaphthalene, 3,4-diaminotoluene, 3,4-diaminobenzoic acid, 1,2-diamino-4-nitrobenzene were obtained from Aldrich.

Synthesis

1,10-phenanthroline-5,6-dione was synthesized according to the literature [3], with a 76% yield. **Dipyrido[2,3-a:2′,3′-c]phenazine** was also synthesized by the literature procedure [4].

11-methyldipyrido[2,3-a:2′,3′-c]phenazine

0.3 g (1.44 mmol) of 1,10-phenanthroline-5,6-dione and 0.423 g (1.43 mmol) of 3,4-diaminotoluene were dissolved in 40 mL of dry ethanol and the mixture refluxed for 2 h. The solution was concentrated to 20 mL and a light brown solid precipitated. Yield: 80%. ν_{max}(KBr)/cm^{-1} 2900–3100 (methyl); λ_{max}(CHCl$_3$)/nm 467; δH (CDCl$_3$)/ppm 9.27, 7.80, 9.62, 8.09, 9.25, 7.76, 9.58, 8.21, 7.73.

11-nitrodipyrido[2,3-a:2′,3′-c]phenazine

0.3 g (1.43 mmol) of 1,10-phenanthroline-5,6-dione and 0.217 g (6.53 mmol) of 1,2-diamino-4-nitrobenzene were dissolved in 40 mL of dry ethanol and the mixture refluxed for 2 h. The solution was concentrated to 20 mL and 0.4 g of a red solid precipitated. Yield 86%. ν_{max}(KBr)/cm^{-1} 1522 and 1350 (NO$_2$); λ_{max}(CHCl$_3$)/nm 441; δH (CDCl$_3$)/ppm 9.35, 7.88, 9.67, 9.30, 9.32, 7.83, 9.63, 8.52, 8.69.

11-aminodipyrido[2,3-a:2′,3′-c]phenazine

0.3 g (0.92 mmol) of 11-nitrodipyrido[2,3-a:2′,3′-c]phenazine and 0.166 g (1.40 mmol) of Sn were dissolved in 8 mL of concentrated HCl and the mixture refluxed for 5 h. The solution was cooled, diluted with water and neutralized to pH 7 with 1 M NaOH. An orange solid precipitated. The solid was purified by Soxhlet extraction with $CHCl_3$. The solvent was removed by a vacuum line and the orange product isolated. Yield 70%. ν_{max}(KBr)/cm^{-1} 1632 and 3421 (NH_2); λ_{max}(CH_3CN)/nm 367 and 384; δH (DMSO)/ppm 9.25, 8.01, 9.59, 7.24, 9.19, 7.93, 9.50, 8.14, 7.59.

11-carboxydipyrido[2,3-a:2′,3′-c]phenazine

0.5 g (2.38 mmol) of 1,10-phenanthroline-5,6-dione and 0.54 g (3.55 mmol) of 3,4-diaminobenzoic acid were dissolved in 40 mL of dry ethanol and the mixture refluxed for 2 h. The solution was concentrated to 20 mL and a pale solid precipitated. Yield 86%. ν_{max} (KBr)/cm^{-1} 1714 (CO_2H); λ_{max} (DMSO)/nm 359 and 376; δH (DMSO)/ppm 9.49, 8.50, 10.01, 9.00, 9.46, 8.47, 9.98, 8.60, 8.68.

$Re(CO)_3(dppz\text{-}NO_2)Cl$

0.20 g (0.61 mmol) of dppz-NO_2 and 0.22 g (0.61 mmol) of $Re(CO)_5Cl$ in 40 mL toluene were refluxed for 6 hours. The orange solid formed was separated by filtration and washed several times with ethyl ether. Yield: 88.3%. ν_{max} (KBr)/cm^{-1} 2031, 1905 (CO); λ_{max} ($CHCl_3$)/nm 361, 296, 284 and 240; δH (DMSO)/ppm 9.67, 9.65, 8.39, 8.35, 9.92, 9.67, 9.34, 8.83, 8.76.

$Re(CO)_3(dppz\text{-}CO_2H)Cl$

0.1 g (0.3 mmol) of dppz-COOH and 0.11 g (0.3 mmol) of $Re(CO)_5Cl$ in 50 mL toluene were refluxed for 15 hours. A yellow precipitate was formed. The mixture was cooled to room temperature and the solid separated by filtration and washed several times with ethyl ether. Finally, the solid was dried in an oven at 60°C. Yield: 87.6%. ν_{max}(KBr)/cm^{-1} 2030, 1939 and 1907 (CO); λ_{max}($CHCl_3$)/nm 364, 296, 282 and 240; δH (DMSO)/ppm 9.64, 9.61, 8.29, 8.27, 9.70, 9.66, 8.86, 8.54, 8.43.

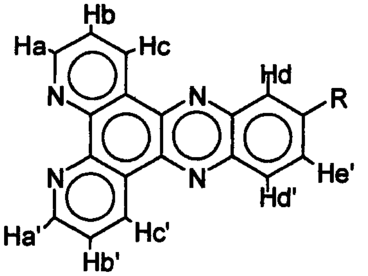
$Re(CO)_3(dppz\text{-}NH_2)Cl$

0.15 g (0.5 mmol) of dppz-NH_2 and 0.18 g (0.5 mmol) of $Re(CO)_5Cl$ in 40 mL toluene were refluxed for 10 hours. The solution was concentrated to half its volume, the solid filtered off, and washed several times with ethyl ether. Yield: 38.2%. ν_{max}(KBr)/cm^{-1} 2023, 1895 (CO); δH (DMSO)/ppm 9.57, 9.50, 8.21, 8.28, 9.89, 9.74, 7.26, 8.34, 7.67.

RESULTS AND DISCUSSION

^{1}H-NMR

Independent of the fragments considered to "build" dppz, the protons of interest are the ones on the bpy or phen fragment (Ha, Hb, Hc, Ha′, Hb′, Hc′) and the ones on phenazine or quinoxaline fragment (Hd, Hd′, He′). The presence of a substituent in the dppz ligand phenazine fragment causes a loss in symmetry as compared to unsubstituted dppz.



R = CH_3, NO_2, COOH, NH_2

The magnetic inequivalence thus introduced affects the phenazine fragment protons and the bpy fragment protons, although to a different extent. As a consequence, the ^{1}H-NMR spectra of the dppz-R ligands show a more complex pattern than of the unsubstituted dppz. Figure 1 shows the spectra for R = CH_3 and R = NO_2 compared to R = H. The Hd, Hd′ and He′ protons are more affected, as expected. Table I collects the corresponding information for all R substituents studied. As the donating properties of the R substituent increase a high field displacement is observed.

$$NO_2 < COOH < H < CH_3 < NH_2 \qquad (1)$$

The *ortho* protons are differently affected by the R substituent. A downfield displacement of 0.94 ppm for the Hd proton is observed for an electronic acceptor substituent, R = NO_2, compared to R = H. Conversely, the resonance shifts 0.27 ppm high field if the substituent is an electron donor, as CH_3. The other *ortho* proton, He′, is less affected. This effect is corroborated by the minimum displacement of the *meta* proton, Hd′, where the

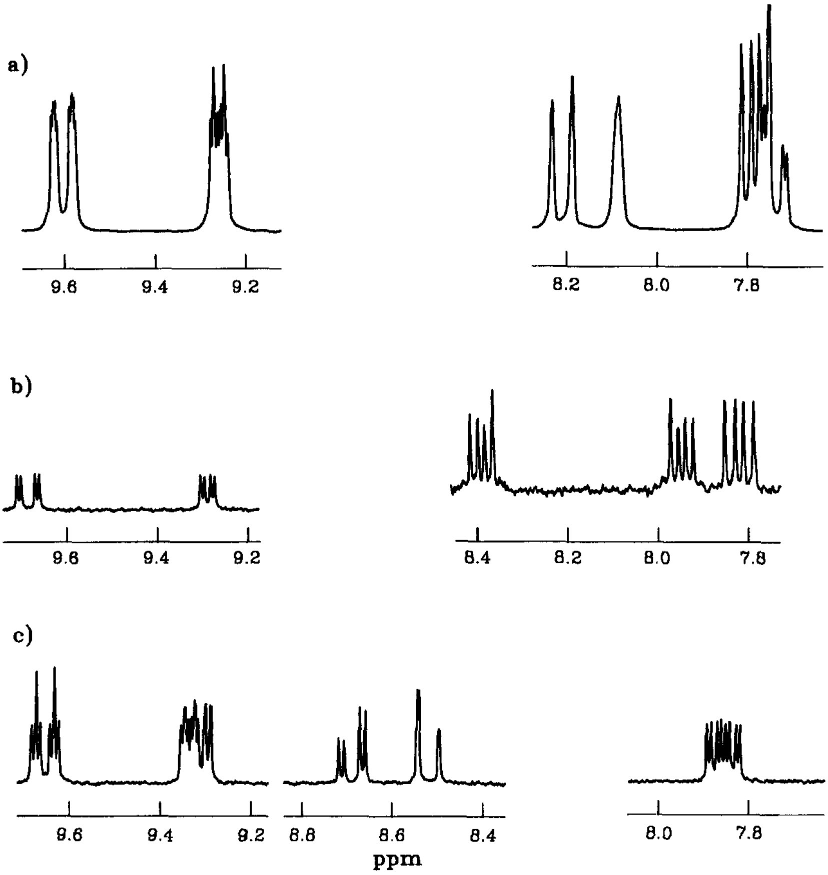


FIGURE 1 ^{1}H-NMR spectra for **a.** dppz, **b.** dppz-CH_3 and **c.** dppz-NO_2.

variation – for all R substituents – is less than ± 0.3 ppm. The behavior observed correlates well with the total charge on the carbon atoms bound to the protons. These charges were calculated by semiempirical PM3 methods and are also shown in Table I. A linear relation with excellent correlation coefficients between chemical shift and carbon atom charge is observed for Hd and He′, Figure 2. The variation of the chemical shifts of these protons by varying R can therefore be interpreted as an electronic effect, induced by the different electron donating or electron-withdrawing capacities of the R substituents. This fact was further corroborated by comparing the experimental chemical shifts with the theoretical values. The calculations were done by considering the dppz phenazine fragment, and using data base information [5a] for its different proton chemical shifts. The shifts expected

TABLE I Chemical shifts δ for dppz-R ligands[a]

R	*Ha*	*Hb*	*Hc*	*Hd*	*He*	*Ha'*	*Hb'*	*Hc'*	*Hd'*	*He'*
NO_2[b]	9.35 (0.150)	7.88 (−0.026)	9.67 (0.045)	9.30 (0.03)	–	9.32 (0.151)	7.83 (−0.027)	9.63 (0.046)	8.52 (−0.0.15)	8.69 (0.0055)
CO_2H[c]	9.49 (0.148)	8.50 (−0.0.28)	10.01 (0.044)	9.00 (0.020)	–	9.46 (0.148)	8.47 (−0.029)	9.98 (0.044)	8.60 (−0.020)	8.68 (−0.004)
H[b]	9.28 (0.145)	7.80 (−0.029)	9.65 (0.042)	8.36 (−0.020)	7.93 (−0.016)	9.28 (0.145)	7.80 (−0.030)	9.65 (0.042)	8.36 (−0.020)	7.93 (−0.016)
CH_3[b]	9.27 (0.144)	7.80 (−0.030)	9.62 (0.042)	8.09 (−0.041)	–	9.25 (0.144)	7.76 (−0.030)	9.58 (0.041)	8.21 (−0.016)	7.73 (−0.026)
NH_2[c]	9.25 (0.145)	8.01 (−0.031)	9.58 (0.042)	7.24 (−0.054)	–	9.19 (0.144)	7.95 (−0.030)	9.50 (0.041)	8.14 (−0.013)	7.59 (−0.028)

[a] Electrostatic charge on the corresponding carbon atom in parenthesis.
[b] In $CDCl_3$.
[c] In DMSO.

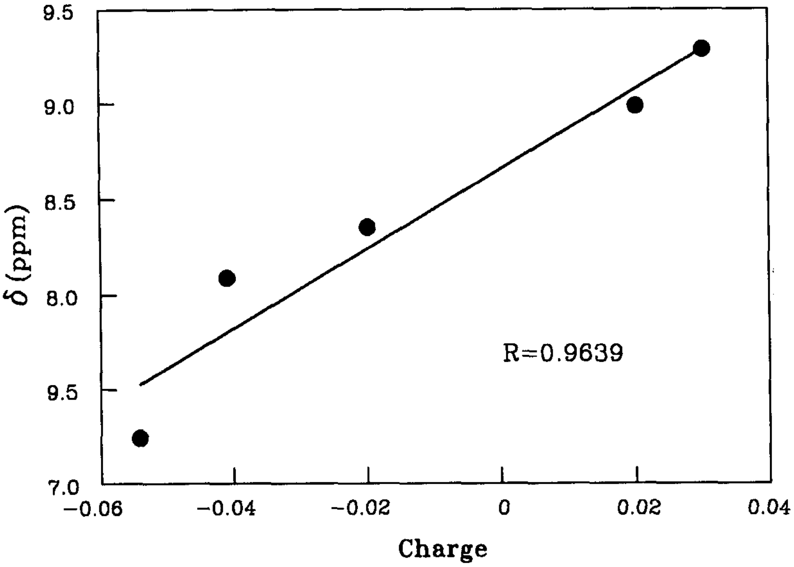


FIGURE 2 Correlation between proton chemical shift and electronic charge on the corresponding carbon atoms.

TABLE II Difference between theoretical and experimental chemical shifts (δ) for phenazine fragment proton in dppz-R

R	*Proton*	*Theoretical δ(ppm)*	*Experimental δ(ppm)*	*Δ (ppm)*
NH_2	Hd	7.51	7.24	0.27
	He′	7.22	7.59	0.37
	Hd′	8.02	8.14	0.12
CH_3	Hd	8.09	8.09	0.00
	He′	7.80	7.73	0.07
	Hd′	8.17	8.21	0.04
CO_2H	Hd	9.06	9.00	0.06
	He′	8.77	8.68	0.09
	Hd′	8.40	8.60	0.20
NO_2	Hd	9.21	9.30	0.09
	He′	8.92	8.69	0.09
	Hd′	8.43	8.52	0.09

for the different R substituents on phenazine were taken from literature as averages based on experimental data [5b, c]. The results are shown in Table II, where Δ represents the difference between theoretical and experimental values. With the sole exception of $R = NH_2$, the coincidence between experimental and theoretical values is very good, pointing again to electronic effects. If the same type of calculation is done with dppz, *i.e.*, instead of phenazine the whole ligand dppz and its corresponding chemical shifts are considered, analogous results are obtained. This last point means that the R displacement values derived for benzene can be applied to predict the behavior of more complex systems such as dppz.

It is important to mention that the $\Delta\delta$ variation is greater for Hd protons than for He′ protons on going from NO_2 to NH_2: 2.06 and 1.1 ppm, respectively. As a consequence of this, for NH_2 the Hd proton appears at higher field than the He′ proton. The carbon atom charge corroborates the assignment.

Contrasting with the behavior of the Hd and He′ protons, the Hd′ protons show no correlation with the carbon atom charge and its behavior must arise from different effects than merely electronic ones. An effect due to the anisotropy of the neighboring phenazine ring heteroatomic N(sp^2) atom can be invoked [6]. This effect would produce a long range deshielding of the Hd′ protons, which would not be evident for Hd, due to the strong influence of the R substituent, as mentioned above. Another point that should not be underestimated is the solvent effect. The ^{1}H-NMR spectra for $R = COOH$ and $R = NH_2$ had to be taken in DMSO, because of insolubility in $CDCl_3$ and other solvents. In contrast, for $R = H$, NO_2 and CH_3, the complexes are insoluble in DMSO. A solvent change does not necessarily affect the chemical shift of different protons in the same manner. As the fluctuation in δ value of Hd′ for different R substituents is considerably smaller than for Hd and He′, the solvent effect can cause a distortion in the δ *vs*. charge correlation in the Hd′ series.

The effect of the R-substituent on the bpy fragment of the dppz ligand is less evident. A general trend according to **(1)** is still observed, but the δ value fluctuation is very small. A relative constancy in the calculated charge density explains this behavior, Table I.

When the dppz-R ligands are coordinated to Re in the Re(dppz-R)$(CO)_3Cl$ complexes, the R-substituent retains the effect on the phenazine fragment protons as predicted by **(1)**, but the whole pattern is displaced to lower field. Nevertheless, the displacement is much more evident for the *meta* (Hd′) proton as compared to R. The bpy fragment protons (Ha, Hb, Hc) are dominated by the effect of coordination. The displacement of the signal to low field as compared to the free ligand is enhanced, reflecting the change in nitrogen atom hybridization because of coordination, with the subsequent deshielding effect on the protons [6]. The behavior of the Hc and Hc′ protons – *para* with respect to the coordinating nitrogens – does not reflect the influence of R. The ^{1}H-NMR data for the complexes are collected in Table III.

TABLE III ^{1}H-NMR chemical shifts (ppm) for Re(CO)$_3$(dppz-R)Cl complexes in DMSO-d_6

Proton	$R=CO_2H$	$R=NO_2$	$R=NH_2$
Ha	9.64	9.67	9.57
Ha′	9.61	9.65	9.50
Hb	8.29	8.39	8.21
Hb′	8.27	8.35	8.28
Hc	9.70	9.92	9.89
Hc′	9.66	9.67	9.74
Hd	8.86	9.34	7.26
Hd′	8.54	8.83	8.34
He	8.43	8.76	7.67

IR

Infrared spectroscopy is important to assure the presence of the different R substituents. As detailed in the experimental section, the characteristic absorption for the R chromophores was observed for all the ligands synthesized. On the other hand, the IR spectra of all the Re(CO)$_3$(dppz-R)Cl complexes showed the typical pattern for the three CO's in *fac* configuration [7]. For example, in Figure 3 the spectrum for Re(CO)$_3$(dppz-CO$_2$H)Cl is shown, with the signals at 2030 cm^{-1}, 1939 cm^{-1} and 1907 cm^{-1}.

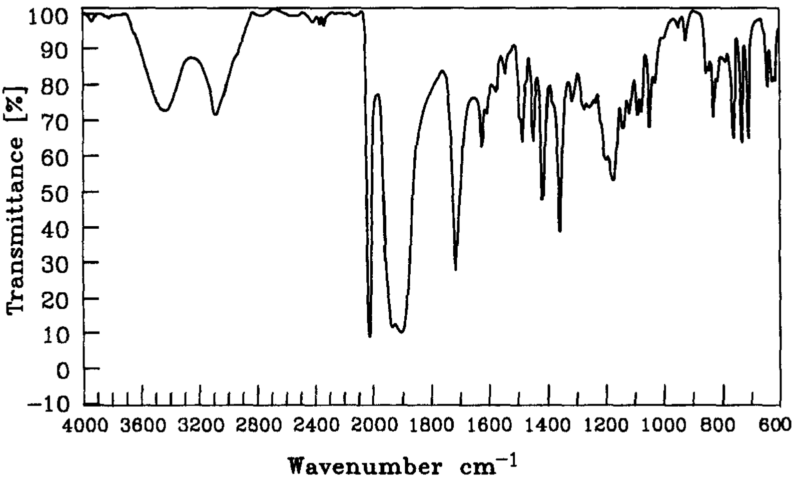


FIGURE 3 IR spectrum for Re(CO)$_3$(dppz-COOH)Cl in KBr pellet.

UV-Vis

The absorption spectra of the free ligands is shown in Figure 4. Two main groups of signals can be observed: in the 350–400 nm region and in the 250–300 region. The band positions seem to be rather insensitive to the R-substituent. This indicates that the substituent affects the energy of both orbitals involved in the transition to a similar extent. For example,

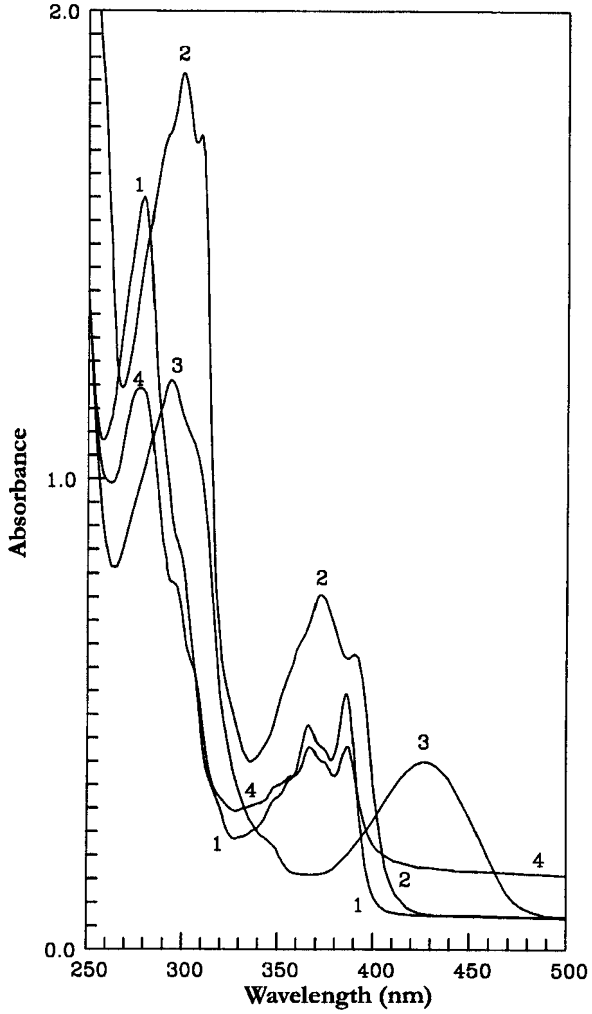


FIGURE 4 UV-Vis electronic absorption spectra for dppz-R type ligands in $CHCl_3$.

$E_{HOMO} = -8.037158\,eV$ and $E_{LUMO} = -1.268035\,eV$ for unsubstituted dppz, while for the acceptor substituent R = COOH, the corresponding energies shift to lower energies: $E_{HOMO} = -8.286321\,eV$ and $E_{LUMO} = -1.555415\,eV$. Nevertheless the $E_{LUMO} - E_{HOMO}$ difference is very similar: 6.77 eV for R = H and 6.73 eV for R = COOH. The calculated spectra correlate reasonably well with the experimental data, and the orbital coefficients involved in the transition assist in assigning the bands. The band close to 400 nm has $n \rightarrow \pi^*$ nature, and is mainly located in the phenazine fragment of the ligand. The rest of the spectrum is dominated by $\pi \rightarrow \pi^*$ bands, that normally involve an electronic transition from one fragment of the molecule to the other. More delocalized π^* orbitals occur for donor R substituents. An $n \rightarrow \pi^*$ band centered in the phenanthroline fragment was only detected theoretically for R = COOH at 372 nm. The shoulder observed close to 340 nm in all ligands is difficult to assign in the experimental spectra. According to the calculations, its ε value is low, normally $1/10\,\varepsilon$ values of the band in the 370 nm region. Finally, for the NO_2-dppz ligand, the experimental spectrum has broader bands than the rest of the ligands, and the high energy pattern is displaced to longer wavelength. The broadness of the bands can be explained by the greater number of theoretical bands observed, all with appreciable ε values. Table IV collects the experimental and calculated absorption bands for all the ligands.

The electronic spectra of the $Re(CO)_3(dppz\text{-}R)Cl$ complexes are dominated by the dppz bands described above. Nevertheless, the coordination to Re is evidenced by MLCT transitions, that appear as a shoulder of the more intense $\pi \rightarrow \pi^*$ ligand bands.

TABLE IV Experimental and calculated absorption bands (nm) in $CHCl_3$ for dppz-R ligands

Ligands	*Experimental (nm)*	*Calculated (nm)*
dppz-NO_2	389,372,307,298	404,378,353,318 306,295,290,282 259,256,243,238
dppz-CO_2H	386,366,276	403,372,342,274
dppz	–	402,372,338,267
dppz-CH_3	385,366,274	401,378,338,303 303,294,292,271 266,248,235,234
dppz-NH_2	430,425,292	400,388,340,305 296,293,277,266 251,239,235

TABLE V Experimental $E_{1/2}$ values compared to E_{LUMO}

R	$E_{1/2}^{1}(mV)$	$E_{1/2}^{2}(mV)$	$E_{LUMO}(eV)$
NO_2	−655	−1178	−1.999369
COOH	≈ −700(sh)	−1183	−1.555415
H	−1800[a]	−1180[a]	−1.268035
CH_3	−1880	−1180	−1.215992
NH_2	−1730	−1345	−1.219362

[a] Reference [8].

Electrochemistry

The cyclic voltammograms of the dppz-R series of ligands show a reversible reduction at *ca.* −1100 mV *vs.* SCE in DMF. A second reduction is observed, that is more sensitive to R substituents. For R = COOH, the $E_{1/2}^{1}$ process is only detectable as a shoulder, but in a position that correlates well with its acceptor properties. Both reductions involve π^* orbitals [8]. Table V gives the experimental $E_{1/2}$ values and the corresponding E_{LUMO}. There is no correlation between $E_{1/2}^{1}$ or $E_{1/2}^{2}$ and the LUMO energy.[1] The dependency of $E_{1/2}^{1}$ on R indicates that the charge density of this orbital involves mainly the ring where R is a substituent, while the constancy of $E_{1/2}^{2}$ would indicate that the orbital participating in this case does not involve this ring. The absence of correlation between $E_{1/2}^{1}$ and the LUMO energy is understandable, in the sense that the LUMO nature changes: for acceptor substituents it corresponds to the orbital involved in $E_{1/2}^{1}$, while for donor substituents it corresponds to the orbital involved in $E_{1/2}^{2}$. Theoretical calculations corroborate these observations: for the acceptor substituents the LUMO electron density involves the region close to the R position, while for the donor substituents the LUMO electron density is delocalized over the whole ligand. This delocalization also helps to understand the enhanced reversibility of $E_{1/2}^{2}$ in regard to $E_{1/2}^{1}$.

CONCLUSION

A substitution on the phenazine fragment of dppz-type ligands affects mainly the environment close to the substituent position, but its effect on remote ligand positions is less evident. This can be concluded mainly from

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[1] The numbering of the $E_{1/2}$ values was done in regard to the first member of the series, $R = NO_2$.

the ^{1}H-NMR and electrochemical data. Therefore, the effect of R on the coordination capacity of the ligand is limited.

Acknowledgments

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