Inorganica Chimica Acta, 108 (1985) L25–L28

Chromophore Selective Resonance Raman Effect in some Heme Model Compounds

HENRIQUE E. TOMA, LUIZ A. MORINO and
PAULO S. SANTOS

Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, S.P., Brazil

Received August 19, 1985

Resonance Raman (RR) spectroscopy has been successfully employed to probe the electronic and structural properties of many biologically relevant molecules [1–3]. In this respect, RR studies of model systems such as the metalloporphyrins and metal diimine complexes [4–8] are contributing to a better understanding of the relationship between the Raman spectra and the electronic absorption spectra of the biomolecules.

Recently, the RR spectra of the bis(pyridine) adducts of several metalloporphyrins have been reported [9] with excitation through the Soret, and α, β bands of the absorption spectra. In general, the excitation profiles for the porphyrin vibrations agree well with theoretical models incorporating vibronic coupling of two excited states, whereas for the pyridine moiety, a direct metal-to-pyridine excitation at the corresponding charge-transfer (CT) band has been suggested [4, 9].

In this work we have investigated the RR spectra of two low molecular weight heme model compounds, namely $[Fe(Hdmg)_2(py)_2]$ and $[Fe(Hdmg)_2(dmpz)_2]$, where Hdmg = dimethylglyoximato ion, py = pyridine and dmpz = 2,6 dimethylpyrazine. These complexes are suitable for comparative purposes, and have stimulated our interest because of the selective enhancement which we observed for the axial and equatorial ligand vibrations, using exciting radiations in resonance with the corresponding metal-to-ligand CT transitions. To our knowledge, this kind of selectivity associated with CT excitations in different chromophores, has never been reported before.

Experimental

The $[Fe(Hdmg)_2(py)_2]$ and $[Fe(Hdmg)_2(dmpz)_2]$ complexes were synthesized from iron(II) acetate and the corresponding ligands (Aldrich) by the method of Pang and Stynes [10]. *Anal.* Calc. for $FeC_{18}N_6H_{24}O_4$: C, 48.66; N, 18.92; H, 5.90. Found: C, 48.62; N, 19.10; H, 5.43. Calc. for $FeC_{20}N_8H_{30}O_4$: C, 47.82; N, 22.31; H, 6.02. Found: C, 47.83; N, 22.55; H, 6.00.

The electronic spectra of the complexes were recorded on a Cary 17 or a Hewlett-Packard 8451 diode-array spectrophotometer. RR spectra were recorded on a Jarrell-Ash instrument using Spectra Physics argon and kripton ion lasers. The complexes are air stable in solid form, but unstable with respect to dissociation and oxidation in chloroform and similar solvents. The visible spectra of the complexes were obtained with the solid suspended in Nujol, or dissolved in chloroform, under argon atmosphere, in the presence of at least five times excess of the N-heterocyclic ligands. Raman spectra were obtained with the solids dispersed in compressed pellets with a supporting medium of sodium sulfate (1 mg of iron complex to 100 mg of sodium sulfate). The measurements were carried out with a spinning cell, to avoid local heating and decomposition of the iron complexes. The relative intensities were measured as peak heights relative to the sulfate Raman band at 994 cm^{-1}. The evaluation of the depolarization ratios for the Raman peaks were precluded by the photodecomposition of the complexes in solution.

Results and Discussion

The electronic spectra of the bis(dimethylglyoximato)iron(II) complexes with aromatic N-heterocyclic ligands consist of two characteristic bands in the visible region, associated with CT transitions form the metal ion to the axial and equatorial ligands [11]. A systematic study [12] on about thirty derivatives has shown that the energies of the axial CT transitions follow very closely the trends in the electron affinities of the N-heterocyclic ligands, varying for instance, from 25×10^3 to 18×10^3 cm^{-1} for the 4-tertbutyl pyridine and the 4-formyl pyridine complexes, respectively. The equatorial CT transitions are less influenced by the substituents at the N-heterocyclic ligands, and span a relatively small range of energies, e.g. 19×10^3 to 21×10^3 cm^{-1}, for the previous complexes. Additional weak absorption bands or shoulders may be detected at 26×10^3 and 21×10^3 cm^{-1}, due probably to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ ligand field transitions, as observed in many related species [13].

In the case of the $[Fe(Hdmg)_2(py)_2]$ complex the Fe-to-py and Fe-to-Hdmg CT bands are well separated, with absorption maxima at 410 nm (24.4×10^3 cm^{-1}) and 518 nm (19.5×10^3 cm^{-1}), and absorptivities of 7.8×10^3 and 9.0×10^3 M^{-1} cm^{-1}, respectively, in chloroform solutions. These CT bands are observed at 414 and 520 nm, respectively in the solid complex, as shown in Fig. 1, A.

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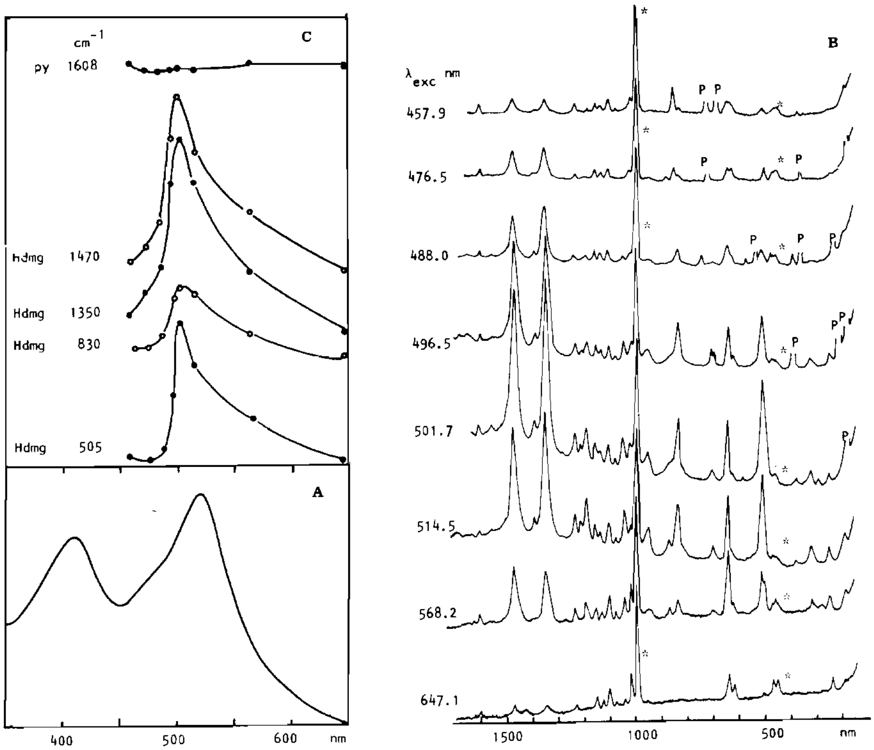

Fig. 1. Electronic absorption spectrum of [Fe(Hdmg)$_2$(py)$_2$] in Nujol (A), and the corresponding RR spectra obtained with excitation at several wavelengths (B). Typical RR enhancement profiles for py and Hdmg vibrational modes are shown in (C).

Raman spectra of the [Fe(Hdmg)$_2$(py)$_2$] complex (Fig. 1, B) were obtained at exciting wavelengths of the Ar$^+$ and Kr$^+$ ion lasers in the range of 457.9 to 647.1 nm. The vibrational frequencies of the Fe(Hdmg)$_2$ moiety were assigned to the peaks at 1470, 1390, 1350, 1190, 1150, 1075, 1045, 945, 830, 700, 635, 505 and 315 cm^{-1} by comparison with the literature data for metal–dioxime complexes [14]. The pyridine vibrations were detected at 1608, 1255, 1045, 1015 and 610 cm^{-1}, corresponding to the totally symmetric modes observed at 1580, 1218, 1029, 992 and 605 cm^{-1} for the free ligand [15] and at 1594, 1214, 1042, 1006 and 632 cm^{-1} for the bis(pyridyl)(octaethylporphyrin)iron(II) complex [9].

The vibrational bands associated with the Hdmg ligand are evidenced in the spectra by the selective RR enhancement at exciting wavelengths close to the Fe-to-Hdmg CT band. Typical RR excitation profiles for Hdmg vibrations can be seen in Fig. 1, C. The most enhanced peaks were observed at 1470, 1350, 830, 505 and 310 cm^{-1}. Normal coordinate analysis for related dioxime complexes has shown that the 1470 and 1350 cm^{-1} vibrational peaks have a large contribution from the C–C and C–N stretching modes. The vibrational peak at 830 cm^{-1} contains nearly equivalent contributions from the N–O and C–CH$_3$ stretching modes. The peaks at 505 and 310 cm^{-1} have a strong Fe–N stretching character, with minor contributions from the C–CH$_3$ stretching and C–C–CH$_3$ bending modes. Therefore, all the groups showing significant RR enhancement belong to the Fe(Hdmg)$_2$ chromophore, which is responsible for the absorption band at 520 nm. The pyridine vibrations are not enhanced within the excitation profile of the Fe(Hdmg)$_2$ chromophore; however, a small enhancement seems to occur at 457.9 nm, suggesting a pre-resonance effect from the Fe-to-py CT band at 410 nm.

We have been particularly interested in the RR spectra of the [Fe(Hdmg)$_2$(dmpz)$_2$] complex because of the strong overlap between the Fe-to-Hdmg and Fe-to-dmpz CT bands, as shown in Fig. 2, A. Gaussian analysis in this case is consistent with two bands at 486 (20.57×10^3 cm^{-1}) and 456 nm (21.93×10^3 cm^{-1}) in chloroform solutions, or at 514 and 473 nm, in the solid state. The assignment of these two bands is not so straightforward as in the pyridine complex, due to their similar energies.

RR spectra of the [Fe(Hdmg)$_2$(dmpz)$_2$] complex are shown in Fig. 2, B. The peaks observed at 1590, 1415, 1160, 1110 and 1025 cm^{-1} were assigned to totally symmetric vibrational modes of the dmpz ligand, based on literature data for several pyridine and pyrazine species [16, 17]. These peaks are strongly enhanced, with a single maximum at 500 nm in the excitation spectra, coinciding with the low energy CT band, as shown in Fig. 2, C. On the other hand,

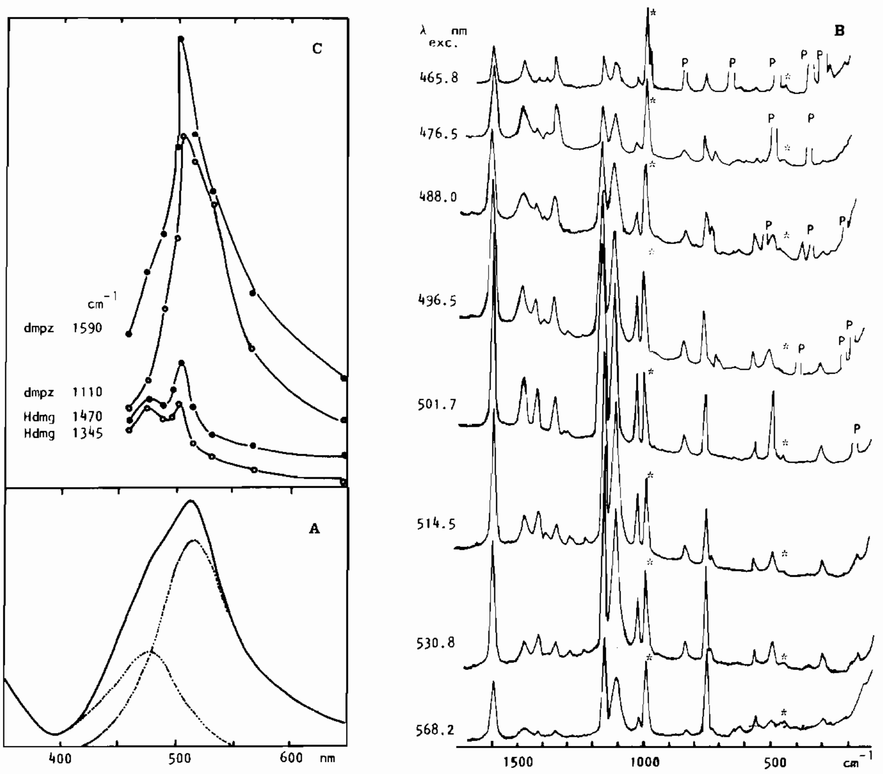

Fig. 2. Electronic absorption spectrum of $[Fe(Hdmg)_2(dmpz)_2]$ in Nujol (A), and the corresponding RR spectra obtained with excitation at several wavelengths (B). Typical RR enhancement profiles for dmpz and Hdmg vibrational modes are shown in (C).

the high energy CT band is located near the minimum in the RR excitation profiles.

In the cases where a single excited state is involved, the RR enhancement is associated with a Franck–Condon mechanism, as expressed by the A term in the formalism of Albrecht and Hutley [18]. The vibrations subject to resonance enhancement are the totally symmetric ones involved in the mixing of the ground and excited states. Therefore, according to the RR excitation profiles for the dmpz ligand, the low energy band should be ascribed to the Fe-to-dmpz CT transition.

The vibrational frequencies of the $Fe(Hdmg)_2$ moiety were assigned on a comparative basis, to the peaks at 1470, 1345, 830, 498 and 300 cm^{-1}. The RR enhancement observed in this case is smaller than that for the axial ligands, and many of the expected vibrational bands of Hdmg are masked by the dmpz bands. In the excitation profiles of Hdmg (Fig. 2, C) there are two maxima coinciding with those of the Fe-to-Hdmg and Fe-to-dmpz CT bands. These two maxima are consistent with a mechanism involving vibronic interactions with two excited states, analogous to that expressed by the B term in the Albrecht-Hutley formalism [18]. This kind of mechanism has already been proposed for porphyrin complexes based on the mixing of two π^* levels of the conjugated system. However, the remarkable point in the $[Fe(Hdmg)_2(dmpz)_2]$ system is that the excited states are associated with two different chromophores in the molecule. The vibrational modes of the axial and equatorial ligands are selectively enhanced via the A or B mechanisms, providing an invaluable support to the assignment of the CT spectra of these heme model systems.

Acknowledgements

We thank FAPESP and FINEP for support.

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