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Polarized Specular Reflectance Spectra of the Partially Oxidized Metallophthalocyanines Ni(pc)I and Co(pc)I: Charge-Transfer Transitions in One-Dimensional Conductors

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Polarized single-crystal specular reflectance spectra and their Kramers–Kronig transformations of Ni(pc)I and Co(pc)I show new results in both the visible and ultraviolet needle axis polarizations. The previously assigned I_3^- transition at 20 000 cm^{-1} appears to be nearly covering an $a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*)$ transition in both compounds, which is of interest in interpreting electrical conducting mechanisms in this class of compounds. An additional transition at ~35 000–40 000 cm^{-1} has been assigned as $b_{2u}(\pi) \rightarrow b_{2g}(d_{x^2-y^2})$ in both compounds.

Introduction

Phthalocyanine complexes have been of optical interest since 1927, when copper and iron phthalocyanines were discovered inadvertently.[2] While their intense colors have made them attractive as textile dyes,[3] they have more recently become of theoretical interest due to their porphyrin-type ring structure and ability to chelate numerous metal ions.[3-18] The observation that a partially oxidized nickel phthalocyanine, Ni(pc)I, was highly one-dimensionally conductive[19] led to increased interest in this class of compounds. One-dimensional conductivity has since been observed in H_2(pc)I,[20] Co(pc)I,[21] Cu(pc)I,[22] and Ni(pc)Br,[23] in which M(pc) has been oxidized to +1/3 in all cases. Temperature-dependent conductivity, magnetic susceptibility, thermoelectric power, and EPR data on Ni(pc)I[19] and Co(pc)I[21] show the former to be a metallic conductor with partial oxidation occurring on the pc ring (ring conductivity), to give a five-sixths-filled macrocycle-based valence band. In contrast, Co(pc)I has semiconductor character, with partial oxidation occurring on the metal (metal spine conductivity). In this compound the d_{z^2} band, initially half full, is proposed as the site of one-electron oxidation for every third Co, thus reducing the band filling to one-third. The charge compensation in both cases is by I_3^- ions, whose periodicity apparently causes gaps in the bands at one-third and two-thirds filling, which in the case of Co(pc)I results in its observed semiconductivity.[21] Because the highest energy occupied orbital is the one that becomes oxidized, the explanation has been that in Ni(pc)I the d_{z^2} band is below the HOMO (valence) macrocycle-based $a_{2u}(\pi)$ band and in Co(pc)I it is above this $a_{2u}(\pi)$ band.[21] We are interested in observing charge-transfer transitions involving both metal and ligand orbitals in order to check these suggestions optically. We report here polarized specular reflectance spectroscopy of Ni(pc)I and Co(pc)I with Kramers–Kronig analyses in the UV and visible spectra in order to study their electronic transitions in more detail and to a greater extent than previously possible.[19b,21]

Experimental Section

Single crystals of Ni(pc)I and Co(pc)I were prepared as before,[19,21] and specimens ~0.030 × 0.030 × 1 mm were selected for study. Lattice constants at room temperature were measured for Co(pc)I by using oscillation and Weissenberg photographs with Cu Kα radiation for comparison with those obtained for this material at low temperature.[21]

Polarized specular reflectance spectra were obtained on an instrument described elsewhere in detail[24] from the (010) faces of Ni(pc)I and Co(pc)I with the electric vector aligned both parallel and perpendicular to the needle (*c*) axes of the crystals. Since the complex planes are normal to the *c* axes, these alignments provided polarizations in the out-of-plane and in-plane directions, respectively. Data were collected with an Apple IIe computer linked to a Hewlett-Packard 3000 mini mainframe. Collection at each data point proceeded until the sample mean had a 99% probability of being within 1% of the population mean. The data were then uploaded to the HP3000 for calculation of percent reflectivity relative to an NBS standard mirror and for Kramers–Kronig analysis.[25,26] For the latter calculations, reflectivities beyond our experimental range were based upon literature values for the infrared spectra[19,21] and were approximated for the vacuum ultraviolet spectra so as to produce base lines approaching zero absorbance in regions known to have no absorbance in related systems in the vapor state.[12] Deconvolution was carried out with an interactive Gaussian and Lorentzian analysis program on the HP3000.

Results and Discussion

The lattice constants for room-temperature Ni(pc)I and low-temperature (116 K) Co(pc)I are very similar with the exception of the *c* axis, where $c = 6.488$ Å for Ni(pc)I[19a] and 6.2466 Å for Co(pc)I.[21] To confirm the assumption that this difference is partially due to axial compression at low temperature, the value of *c* was measured by an oscillation X-ray photo of Co(pc)I at room temperature. The value was found to be 6.33 ± 0.05 Å. A 0-level Weissenberg photo of Co(pc)I at room temperature shows little change in the other axial dimensions.

The polarized specular reflectance spectra for both axial and

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(1) (a) Franklin and Marshall College. (b) Northwestern University.
(2) Linstead, R. P. *J. Chem. Soc.* **1934**, 1016.
(3) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 28.
(4) Kasuga, K.; Tstsui, M. *Coord. Chem. Rev.* **1980**, *32*, 67.
(5) Basu, S. *Indian J. Phys.* **1954**, *28*, 511.
(6) Lyons, L. E. *J. Chem. Soc.* **1958**, 1347.
(7) Lyons, L. E.; Walsh, J. R.; White, J. W. *J. Chem. Soc.* **1960**, 167.
(8) Day, P.; Scregg, G.; Williams, R. J. P. *J. Chem. Phys.* **1963**, *38*, 2778.
(9) Gouterman, M.; Wagniere, G. H.; Snyder, L. C. *J. Mol. Spectrosc.* **1963**, *11*, 108.
(10) Fielding, P. E.; MacKay, A. G. *Aust. J. Chem.* **1964**, *17*, 750.
(11) Chen, I. *J. Mol. Spectrosc.* **1967**, *23*, 131.
(12) Edwards, L.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *33*, 292.
(13) Schaffer, A. M.; Gouterman, M.; Davison, E. R. *Theor. Chim. Acta* **1973**, *30*, 9.
(14) Schaffer, A. M.; Gouterman, M. *Theor. Chim. Acta* **1972**, *25*, 62.
(15) McHugh, A. J.; Gouterman, M.; Weiss, C., Jr. *Theor. Chim. Acta* **1972**, *24*, 346.
(16) Fielding, P. E.; MacKay, A. G. *Aust. J. Chem.* **1975**, *28*, 1445.
(17) Lever, A. B. P.; Pickens, S. R.; Minor, P. C.; Licoccia, S.; Ramaswamy, B. S.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800.
(18) Minor, P. C.; Gouterman, M.; Lever, A. B. P. *Inorg. Chem.* **1985**, *24*, 1894.
(19) (a) Schramm, C. J.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702. (b) Martinsen, J.; Palmer, S. M.; Tanaka, J.; Greene, R. C.; Hoffman, B. M. *Phys. Rev. B* **1984**, *30*, 6269.
(20) Inabe, T.; Marks, T. J.; Burton, R. L.; Lyding, J. W.; McCarthy, W. J.; Kannewurf, C. R. *Solid State Commun.* **1985**, *54*, 501.
(21) Martinsen, J.; Stanton, J. L.; Greene, R. L.; Tanaka, J.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 6915.
(22) Ogawa, M. Y.; Martinsen, J.; Palmer, S. M.; Stanton, J. L.; Tanaka, J.; Greene, R. L.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1115.
(23) Palmer, S. M.; Stanton, J. M.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1986**, *25*, 2296.
(24) Desjardins, S. R.; Penfield, K. W.; Cohen, S. L.; Musselman, R. L.; Solomon, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 4590.
(25) Anex, B. G. *Mol. Cryst.* **1966**, *1*, 1.
(26) Kronig, R. de L. *J. Opt. Soc. Am.* **1906**, *12*, 157.

0020-1669/89/1328-0283$01.50/0

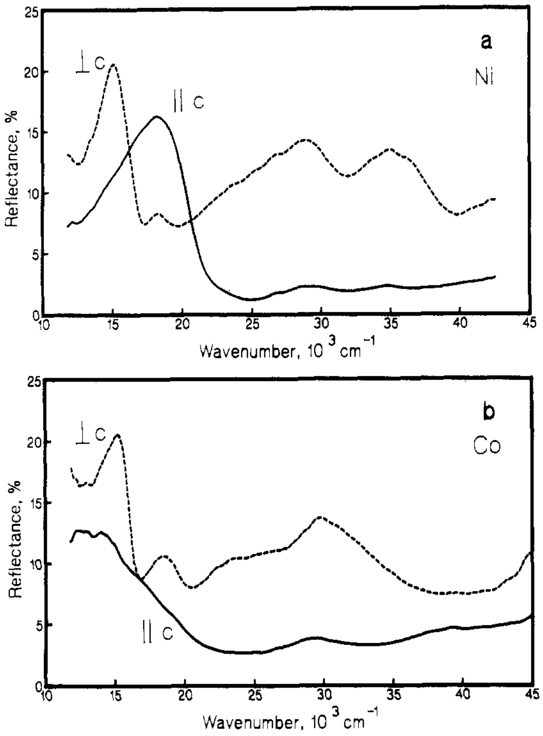

Figure 1. Single-crystal polarized specular reflectance spectra (—, electric vector parallel to the needle axis; ---, electric vector perpendicular to the needle axis (in-plane)): (a) Ni(pc)I; (b) Co(pc)I.

in-plane spectra for Ni(pc)I and Co(pc)I are shown in Figure 1. The reflectances reported are absolute values after comparison with an NBS mirror. After Kramers–Kronig transformation, the absorbances shown in Figure 2 are available. One advantage of absorbance values over reflectances is the ability to evaluate band shapes by using standard deconvolution techniques. In this study the axial polarizations were the most interesting, so these will be discussed first.

Out-of-Plane Spectra. A prominent feature in both the Ni(pc)I and Co(pc)I axial spectra is the absorbance around 15 000–20 000 cm^{-1}. For both compounds, this feature has been previously observed in reflectance and has been assigned as the $\sigma_g \rightarrow \sigma_u^*$ transition (filled nonbonding pσ to unfilled antibonding pσ)[27] in I_3^-.[19,21] The maximum of absorption for Ni(pc)I is 18 700 cm^{-1} and for Co(pc)I is 15 000 cm^{-1} (derived from reflectivity maxima of 18 500 and 13 500 cm^{-1}). This difference in energy has earlier been attributed to the average spacing between iodide ions along the axial direction in Co(pc)I being less than in Ni(pc)I.[21] Further, it is interesting to note that the Kramers–Kronig transformations in Figure 2 show asymmetry in the Ni(pc)I peak and some structure in the Co(pc)I peak, suggesting that more than one transition is represented by each peak. We will thus consider the $\sigma_g \rightarrow \sigma_u^*$ transition in I_3^- in more detail at this point.

Triiodide Transitions. The iodines in both Ni(pc)I and Co(pc)I are, on average, evenly spaced along the *c* axis with an average spacing of 3.24 Å[19a] in Ni(pc)I and 3.17 Å in Co(pc)I, with large values for thermal parameters along the chain, suggestive of positional disorder. The existence of discrete I_3^- units has been demonstrated by using diffuse X-ray scattering.[19a] In addition, the above-mentioned resonance Raman results showing I–I stretches of 107 and 109 cm^{-1} agree well with those for I_3^- in other systems,[28] indicating that the bond strengths are consistent with I_3^-.

The electronic spectrum of I_3^- in the solid state is dependent upon the relative arrangements of the I_3^- units.[27-29] Two arrangements in which I_3^- ions align very close to linear are $(bza)_2{\cdot}HI_3$ and caf$\cdot H_2O \cdot HI_3$,[30] in which the average I–I distances along the chains are 3.23 and 3.24 Å, respectively (bza = benzamide; caf = caffeine). In $(bza)_2{\cdot}HI_3$, the I_3^- units are ordered with I–I distances of 2.93 and 2.92 Å. In the caffeine I_3 crystal, the I–I distance in I_3^- is ~2.92 Å. For both of these crystals, the specular reflectance spectra have prominent peaks polarized along the I_3^- chains at 20 000 cm^{-1}, assigned as $^1\Sigma_g \rightarrow {}^1\Sigma_u^*$ ($\sigma_g \rightarrow \sigma_u^*$), and at 30 000 cm^{-1}, assigned tentatively as a spin–orbit-coupling component of the 20 000-cm^{-1} peak.[28] The geometry and average I–I spacing in Ni(pc)I (3.24 Å)[19] and Co(pc)I (3.17 Å) are nearly identical. Resonance Raman spectra of $(bza)_2{\cdot}HI_3$ and caf$\cdot H_2O \cdot HI_3$ show fundamental I–I stretches at 110[29] and 108 cm^{-1},[28] respectively, which is in good agreement with the values of 107 and 109 cm^{-1} for I_3^- in Ni(pc)I and Co(pc)I.[19,21]

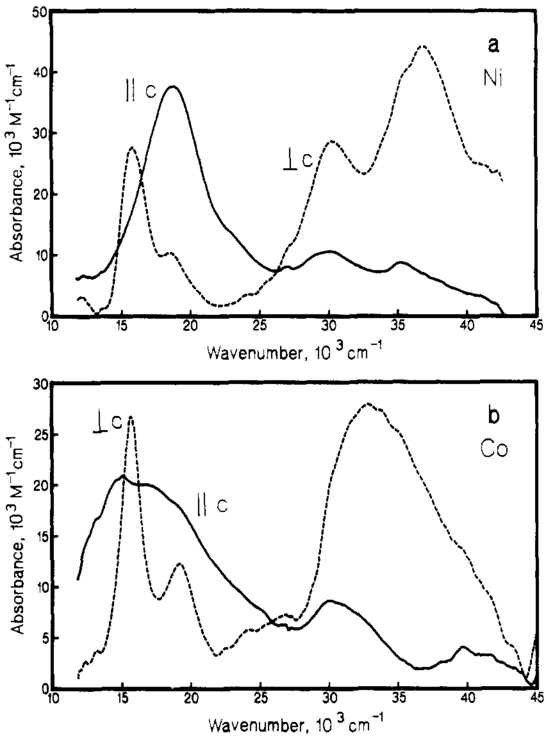

Figure 2. Kramers–Kronig transformed spectra, polarized parallel (—) and perpendicular (---) to the needle axis: (a) Ni(pc)I; (b) Co(pc)I.

It is thus reasonable to expect that the I_3^- groups, in the Ni(pc)I and Co(pc)I crystals, will yield a visible spectrum very similar to that for the benzamide and caffeine triiodides. In fact, however, the maxima of the ~20 000-cm^{-1} peaks in Ni(pc)I and Co(pc)I fall at 18 750 and 15 100 cm^{-1}, respectively. Therefore, before placing a Gaussian peak to represent the $^1\Sigma_g \rightarrow {}^1\Sigma_u^*$ I_3^- transition in this region in Ni(pc)I and Co(pc)I, we examined the relative positions of the $^1\Sigma_g \rightarrow {}^1\Sigma_u^*$ transition and its associated ~ 30 000-cm^{-1} transition in the comparison I_3^--containing crystals tetra-*n*-butylammonium (TBA) triiodide, $(bza)_2{\cdot}HI_3$, and caf$\cdot H_2O \cdot HI_3$.[30] In the last two, the higher energy transition appears very close to 30 000 cm^{-1}, 10 000 cm^{-1} above the corresponding $^1\Sigma_g \rightarrow {}^1\Sigma_u^*$ transition.[28] The TBA salt has a slightly nonlinear arrangement of adjacent I_3^- units, and the $^1\Sigma_g \rightarrow {}^1\Sigma_u^*$ transition is raised to 22 500 cm^{-1}. The higher energy transition follows this shift, appearing at 32 500 cm^{-1}. In Ni(pc)I and Co(pc)I, as shown in Figure 3, there are peaks at 29 950 and 30 100 cm^{-1}. The clearly resolved positions of these peaks suggest that the placement of the $^1\Sigma_g \rightarrow {}^1\Sigma_u^*$ transitions in Ni(pc)I and Co(pc)I should both be at ~20 000 cm^{-1}. We therefore performed Gaussian analyses on the axially polarized spectra of Ni(pc)I and Co(pc)I, targeting 20 000 cm^{-1} for the I_3^- peak in question. The results were peaks at 20 000 and 19 900 cm^{-1} with half-widths of 7000 cm^{-1}, which

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(27) (a) Gabes, W.; Nijman-Meester, M. A. M. *Inorg. Chem.* **1973**, *12*, 589. (b) Gabes, W.; Stufkens, D. J. *Spectrochim. Acta, Part A* **1974**, *30*, 1835.

(28) Mizuno, M.; Tanaka, J.; Harada, I. *J. Phys. Chem.* **1981**, *85*, 1789.

(29) Marks, T. J. *Ann. N.Y. Acad. Sci.* **1978**, 594.

(30) Herbstein, F. H.; Kaftory, M.; Kapon, M.; Saenger, W. *Z. Kristallogr.* **1981**, *154*, 11.

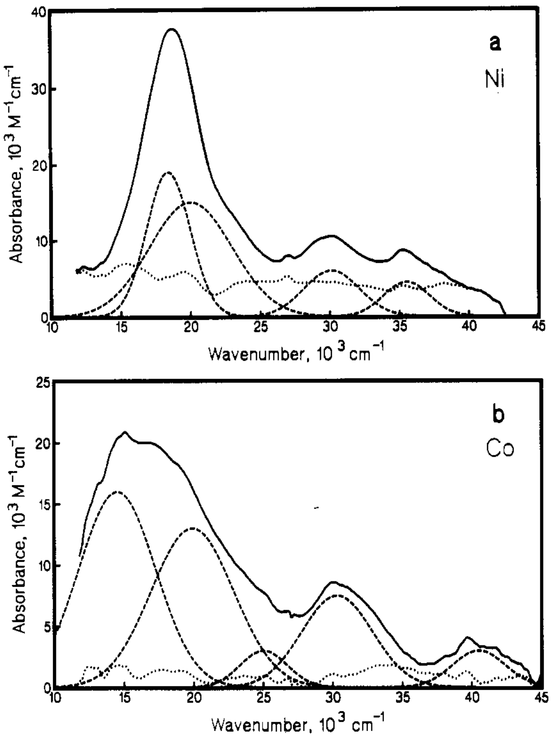

Figure 3. Gaussian analyses of axial polarizations (—, transformed experimental spectrum; ---, Gaussian curve; ···, residual): (a) Ni(pc)I; (b) Co(pc)I.

Table I. Spectra–Structure Correlations in Selected Square-Planar Complexes

compd	M–M spacing, Å	$\bar{\nu}_{\epsilon_{max}}$, 10^3 cm^{-1}	ref
Ni(dmg)$_2$ (soln)	"∞"	23.0	31
Ni(emg)$_2$	4.75	23.0	31
Ni(hept)$_2$	3.60	21.9	31
Ni(dpg)$_2$	3.52	19.6	31
Ni(dmg)$_2$	3.25	18.6	31
Ni(pc)I	3.24[19]	18.4	this work
Co(pc)I	3.17	14.5	this work

are shown, along with other peaks in the spectra and the residuals, in Figure 3. Additional confirmation was sought through relative integrated peak intensities of the 20000-cm^{-1} and the 30000-cm^{-1} peaks in the three comparison I_3^- compounds, but their 250% variation made any comparisons inconclusive. We will thus rely on the 10000-cm^{-1} difference in I_3^- transitions as the basis for this deconvolution. On this basis, then, there appear two significant $\|c$-polarized peaks to the red side of the $^1\Sigma_g \rightarrow {}^1\Sigma_u{}^*$ I_3^- transition: 18400 cm^{-1} in Ni(pc)I and 14500 cm^{-1} in Co(pc)I.

Metal–Ligand Transitions. The apparent peaks at 18400 and 14500 cm^{-1} in Ni(pc)I and Co(pc)I are very interesting, being reminiscent of the low-energy out-of-plane polarized transitions in Ni(dmg)$_2$ and Ni(dpg)$_2$[31] (dmg = dimethylglyoximate and dpg = diphenylglyoximate). Table I summarizes the structural and optical features of interest for these and related compounds.

Ni(pc)I thus seems to follow the trend of Ni(dmg)$_2$ and related compounds in which a shortened stacking distance between complex planes results in a red shift of a transition originally at 23000 cm^{-1} in solvated bis(dimethylglyoximato)nickel. This transition was assigned by Anex and Krist as $^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*,p_z)$).[31] This follows Gray and Ballhausen's molecular orbital scheme for square-planar complexes having unsaturated ligands[32] in which $d_{x^2-y^2}$ is empty in d^8 metals and is well above the remaining d orbitals. The similarity of the M–M stacking distances, ring structures, and peak positions in Ni(dmg)$_2$ and Ni(pc)I leads us to tentatively assign the 18400-cm^{-1} peak in Ni(pc)I also as the $^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*,p_z)$) transition. There is significant additional precedent for the concept of red shifting of out-of-plane transitions upon decreasing the stacking distance, especially in the tetracyano complexes of Ni, Pd, and Pt.[33–36] The unperturbed $a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*)$ transition in phthalocyanines has been calculated with extended Hückel methods to be at 31200 cm^{-1}.[13] Unfortunately there is no suitable phthalocyanine available in which to search for this unperturbed transition. Unoxidized Ni(pc) has a structure dramatically different,[39] with a herringbone arrangement yielding a solid-state environment unsuitable for straightforward comparison. Single molecules of Ni(pc) in the vapor state[12] do not, of course, allow for polarization studies, and the dominant (pc) ring transition at 30100 cm^{-1}, the $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ (Soret) in-plane transition (vide infra), would make an expectedly small[33] out-of-plane transition undetectable.

The corresponding peak in Co(pc)I appears in accord with that in Ni(pc)I, allowing for both a slightly shorter M–M distance and for an expected larger overlap of $4p_z$ orbitals, which in turn mix with the $a_{2u}(\pi^*)$ pc orbitals, thereby lowering the a_{2u} level more than in Ni(pc)I. This peak is thus also tentatively assigned as $^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*,p_z)$), red-shifted by axial perturbations.

The ultraviolet transitions are seen here in partially oxidized metallophthalocyanines for the first time. An axially polarized set of transitions occurs at 35500 cm^{-1} in Ni(pc)I and at 40500 cm^{-1} in Co(pc)I. The large difference in transition energy suggests that this is also a metal-related transition. The ligand-based transitions, as will be discussed in a later section, appear at the same energies in the two compounds. Since the cobalt 3d levels are of a higher energy than those in nickel,[13] it seems appropriate to consider this transition to be a ligand to metal charge-transfer transition. Lever et al. have suggested three LMCT transitions in M(pc) compounds,[17] only one of which is allowed z: $a_{2u}(\pi) \rightarrow a_{1g}(d_{z^2})$. Another possible z-polarized transition would be $b_{2u}(\pi) \rightarrow b_{1g}(d_{x^2-y^2})$.

The $a_{2u}(\pi) \rightarrow a_{1g}(d_{z^2})$ transition has been predicted to appear around 10000 cm^{-1} in unoxidized Co(pc).[17] It would not appear in Ni(pc) since the d_{z^2} orbital is filled[17] and would also not appear in Ni(pc)I since the pc ring rather than the Ni d_{z^2} band is oxidized.[19] Since the peaks in question are in both complexes and are far above 10000 cm^{-1}, it may be assumed that they are not the $a_{2u}(\pi) \rightarrow a_{1g}(d_{z^2})$ transition.

This leaves the $b_{2u}(\pi) \rightarrow b_{1g}(d_{x^2-y^2})$ transition. The $3d_{x^2-y^2}$ orbital in Co(pc) has been estimated to be 5370 cm^{-1} above that in Ni(pc).[13] Predicted differences for other 3d-based orbitals between Co and Ni range from 806 to 2150 cm^{-1}.[13] Thus, the experimental difference of 5000 cm^{-1} clearly points to the $3d_{x^2-y^2}$ orbital as being the terminal orbital in the Co(pc)I and Ni(pc)I 40500- and 35500-cm^{-1} peaks. An early calculation by Gouterman et al.[9] places the $3b_{2u}$ orbital 1850 cm^{-1} below the $4a_{2u}$ orbital, and a more recent calculation[13] places $4a_{2u}$ 30700 cm^{-1} below the Ni $b_{1g}(d_{x^2-y^2})$ orbital in Ni(pc). If configuration interaction[15] is ignored, the estimated transition energy for $3b_{2u} \rightarrow b_{1g}(d_{x^2-y^2})$ is thus 32550 cm^{-1}. This is in good agreement with the peak at 35500 cm^{-1} in Ni(pc)I. That peak and the corresponding one at 40500 cm^{-1} in Co(pc)I may thus be assigned as $3b_{2u} \rightarrow b_{1g}(d_{x^2-y^2})$.

In-Plane Transitions. The visible regions of the in-plane spectra are identical for both Ni(pc)I and Co(pc)I (Figure 4) and show the familiar "Q" transition at 15700 cm^{-1} assigned as $a_{1u}(\pi) \rightarrow e_g(\pi^*)$,[11–14] one of the HOMO's to the LUMO,[13] and the accompanying peak at ~18700 cm^{-1}, about which there is some

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(31) (a) Anex, B. G.; Krist, F. K. *J. Am. Chem. Soc.* **1967**, *89*, 6114. (b) Krist, F. K. Ph.D. Dissertation, Yale University, 1966.

(32) Gray, H. B.; Ballhausen, C. J. *J. Am. Chem. Soc.* **1963**, *85*, 260.

(33) Musselman, R. L.; Anex, B. G. *J. Phys. Chem.* **1987**, *91*, 4460.

(34) Moreau-Colin, M. L. *Struct. Bonding* **1972**, *10*, 167 and references therein.

(35) Yersin, H.; Gliemann, G. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 539.

(36) Musselman, R. L. Manuscript in preparation.

(37) Robertson, J. M.; Woodward, I. *J. Chem. Soc.* **1937**, 219.

(38) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1695.

(39) Hochstrasser, R. M. *Molecular Aspects of Symmetry*; Benjamin: New York, 1966; Chapter 10.

(40) Liou, K.; Jacobsen, C.; Hoffman, B. M. Manuscript in preparation.

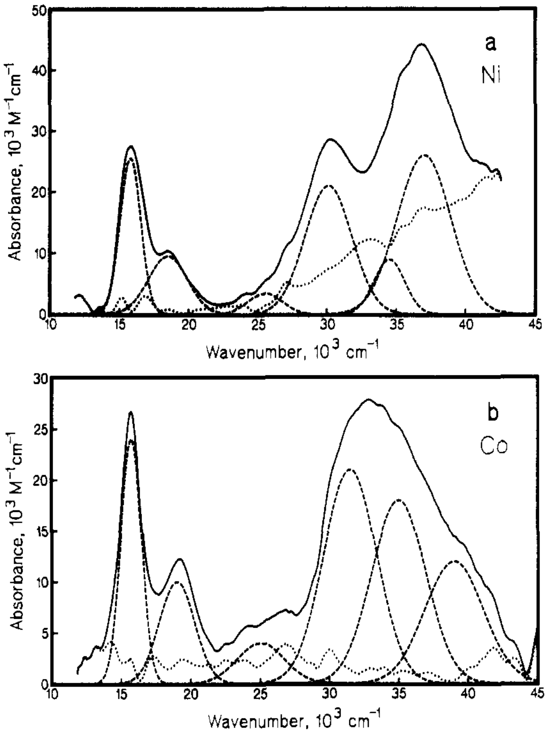

Figure 4. Gaussian analyses of in-plane polarizations (—, transformed experimental spectrum; - - -, Gaussian curve; ···, residual): (a) Ni(pc)I; (b) Co(pc)I.

disagreement of assignment. This latter peak has been assigned in M(pc) as a vibronic component of the Q band[38] and as a splitting of Q due to a lowered site symmetry.[8] In Ni(pc) and Co(pc) the energy difference is close to 2000 cm^{-1}.[10] In Ni(pc)I and Co(pc)I the differences are 3000 and 3700 cm^{-1}, respectively. Since partial oxidation removes an electron from orbitals involved in bonding rather than antibonding, it is not likely that it would result in an increase in the vibrational frequency that may have mixed with the Q band. Factor group splitting[39] is possible in Ni(pc)I and Co(pc)I as well as in Ni(pc) and Co(pc). The latter case involves changing a D_{4h} point group to a D_2 site group due to the herringbone arrangement of M(pc)'s, and the present case has a D_{4h} point group to C_4 site group change. The interplanar distances are similar (3.22 Å for Co(pc) vs 3.17 Å for Co(pc)I), and with the greater area of approach for the straight-stacked M(pc)I's, it is reasonable to expect a greater factor group splitting for the M(pc)I's. The 3000- and 3700-cm^{-1} splitting observed in Ni(pc)I and Co(pc)I around ~18 700 cm^{-1} is consistent with this expectation, and we thus tentatively assign the ~18 700-cm^{-1} peaks in Co(pc)I and Ni(pc)I as symmetry-split Q satellites.

The peak at 30 100 cm^{-1} in Ni(pc)I appears to be the Soret-equivalent band (B band), $a_{2u}(\pi) \rightarrow e_g(\pi^*)$, which appears at 30 500 cm^{-1} in vapor-state Ni(pc).[12] The equivalent peak in Co(pc)I is not resolved, so we have estimated its position as shown in Figure 4b to be at 31 600 cm^{-1} through comparison with the B band in vapor-state Co(pc) at 32 000 cm^{-1} [12] and the difference in B-band energies in the Ni(pc), Ni(pc)I pair.

The small Gaussian peaks at ~25 000 cm^{-1} in the in-plane spectra of both compounds (Figure 4) are marginal but are hard to ignore, especially in the case of Co(pc)I. The similarity in energies suggests a ligand-based transition, but according to Gouterman's scheme[13] and the estimated energy for $b_{2u}(\pi)$ noted above, the only remaining x,y-polarized transition in this region, $b_{2u}(\pi) \rightarrow e_g(\pi^*)$, should appear at a slightly higher energy than the B band rather than 5000 cm^{-1} lower. The identities of these features, if in fact real, remain uncertain.

The remaining high-energy intensity in both systems around 35 000–40 000 cm^{-1} appears to consist of two transitions in each, which are consistent with peaks observed in the vapor state[12] and assigned as $e_g(d_{xz,yz}) \rightarrow b_{1u}(\pi^*)$ and $e_g(d_{xz,yz}) \rightarrow b_{2u}(\pi^*)$, both polarized in-plane.

Conclusions

The in-plane spectra for Ni(pc)I and Co(pc)I are consistent with earlier assignments of x,y transitions in the corresponding unoxidized compounds. The out-of-plane spectra, however, show a peak in the ultraviolet spectra not previously observed in M(pc)'s because of overlap by the more intense in-plane transitions; they appear to reveal an additional transition in the visible region near the previously identified I_3^- transition.

This latter transition, which we tentatively assign as $a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*,p_z)$, has been observed in nonconducting precursors[33-36] to partially oxidized potassium tetracyanoplatinates (KCP) but not in KCP's themselves.[41] It appears that this molecular transition, which can also be characterized as an interband transition,[42] is not hidden in Ni(pc)I and Co(pc)I by the high reflectivity of an intraband transition as it may be in KCP. Since in Ni(pc)I it is the pc that is oxidized rather than Ni^{2+}, one might expect a double-humped absorption characteristic of one-dimensional bands between d_{z^2} and p_z bands.[42] However, the intrinsic broadening of discrete electronic transitions apparently masks such features. In Co(pc)I, where the partial oxidation and conductivity have been found to be metal chain based[21] instead of π ring based as in Ni(pc)I,[19] the one-third filling of the d_{z^2} band would lead to a single peak for the transition to an $a_{2u}(\pi^*,p_z)$ band. The especially interesting feature is that we seem to be observing a transition from the d_{z^2} band responsible for d_{z^2} metal spine semiconductivity in Co(pc)I.

We are currently pursuing other conductors with porphyrinic ligands, including both metal-free and iodine-free systems, to clarify the nature of the ~20 000-cm^{-1} needle-axis-polarized absorption and the role of solid-state perturbations on related single-molecule transitions.

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(41) Musselman, R. L.; Williams, J. M. *J. Chem. Soc., Chem. Commun.* **1977**, 186.

(42) Cox, P. A. *The Electronic Structure and Chemistry of Solids*; Oxford University Press: Oxford, England, 1966; Chapter 4.