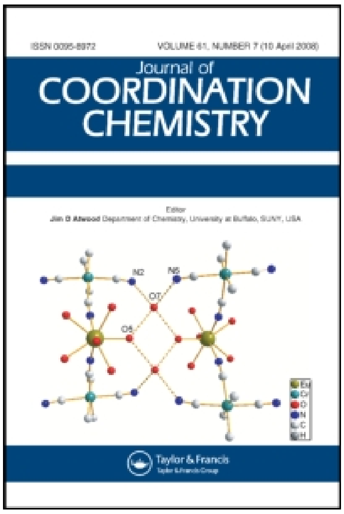

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W. J. Barreto[a]; P. S. Santos[b]
[a] Departamento de Quimica, Universidade Estadual de Londrina, Londrina, PR, Brasil [b] Instituto de Quimica, Universidade de So Paulo, So Paulo, SP, Brasil

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PREPARATION, ELECTRONIC, IR AND RESONANCE RAMAN SPECTRA OF TWO NICKEL DMIT-PIPERIDINE MIXED COMPLEXES

W.J. BARRETO*

Departamento de Quimica, Universidade Estadual de Londrina, CP.6001, Londrina, PR, Brasil

and P.S. SANTOS

Instituto de Quimica, Universidade de São Paulo, CP.20780, São Paulo, SP, Brasil

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The preparation of the mixed complexes $[Ni(dmit)_2(piperidine)_2][NBu_4]$ and $[Ni(dmit)(pip)_2]$ are reported for the first time and their electronic, IR and resonance Raman spectra are presented. The results suggest that previous assignments for bis-dmit metal complexes are not correct. In particular, the band previously assigned to an internal transition of the ligand in the visible region is now shown to originate from an interligand transition, involving molecular orbitals extensively delocalized over the molecule.

KEYWORDS: Dithiolenes, dmit, piperidine, resonance Raman, nickel complexes

INTRODUCTION

Dithiolenes have been extensively investigated over recent years, due to the fact that several of their complexes have shown appreciable values of conductivity in the solid state.[1] In addition, several such complexes display non-linear optical properties, thus making their investigation even more attractive. In addition, dithiolenes are remarkable in their ability to stabilize transition metal ions in several oxidation states, normally impossible with other ligands. One of the most thoroughly investigated dithiolenes is dmit, the anion of 4,5-dimercapto-1,3-dithiole-2-dithione. Characteristic of dithiolene complexes is the presence of rather strong absorption bands at abnormally low energies ($\varepsilon = 2 - 4 \times 10^4\ M^{-1}\ cm^{-1}$ and λ_{max} above 700 nm). Depending on the particular complex considered it is also possible to detect much weaker d-d transitions at higher energies. The remaining transitions present in the UV-VIS region are still rather controversial with respect to origin. In particular, the species $[M(dmit)_2]^{n-}$, where n = 0, −1, −2 and M = Ni, Pd, Pt or Cu have been the subject of several publications[2,3,4] but assignment of electronic spectra is still open to debate. In a previous publication we made use of resonance

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* Author for correspondence.

Raman spectroscopy to probe the assignment for the species $[Zn(dmit)_2]^{2-}$ and $[Ni(dmit)_2]^{2-}$, showing that the intense band in the visible is in fact of a charge transfer nature.[5]

In order to better understand the nature of such transitions, we have prepared and investigated dmit complexes containing piperidine as a counter-ligand. In particular, for $[Ni(dmit)_2(pip)_2]^-$ (I), Figure 1a, an interligand transition involving both dmit moieties is possible, while for the species $[Ni(dmit)(pip)_2]$ (II), Figure 1b, due to the characteristics of the saturated heterocyclic counter ligand, such a

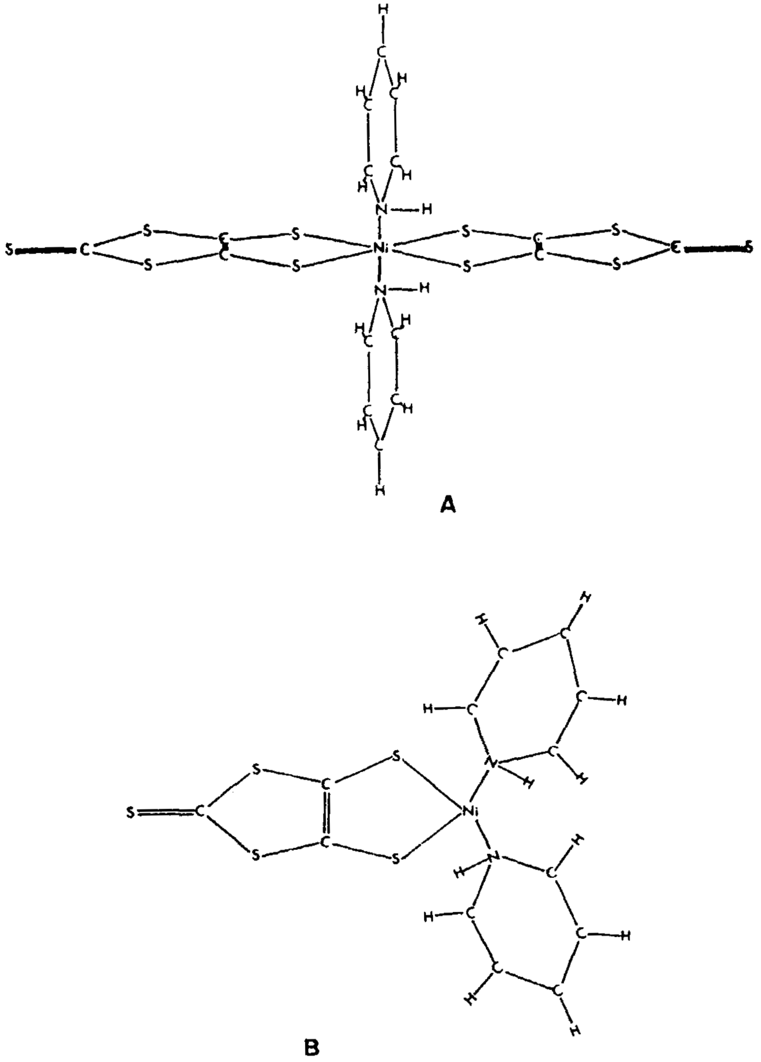

Figure 1 Proposed structure of (a) $[Ni(dmit)_2(piperidine)_2]^-$ and (b) $[Ni(dmit)(piperidine)_2]$.

transition would not be feasible. Consequently a comparative study of compounds **I** and **II** by means of electronic and resonance Raman spectroscopies was expected to yield additional information on the nature of electronic transitions observed in dmit complexes.

EXPERIMENTAL

Chemicals

$[NBu_4][Ni(dmit)_2(pip)_2]$ was prepared by reacting *ca* 0.314 g of $[NBu_4]_2[Zn(dmit)_2]$, prepared according to Steimecke et al.,[6] dissolved in 20 cm^3 of CH_3CN with *ca* 0.03 g of piperidine, with the subsequent dropwise addition of 0.09 g of $NiSO_4 \cdot 6H_2O$ dissolved in 5 cm^3 of water. Stirring and heating (60°C) was maintained for *ca* 3 hours and then the reaction mixture left to stand for 24 hours, followed by evaporation of the solvent. The residue was dissolved in hot ethanol and filtered; by cooling red crystals were obtained. Anal; calcd: C, 44.5; N, 4.8; H, 6.7%. Found: C, 44.8; N, 4.4; H, 6.8%.

$[Ni(dmit)(pip)_2]$ was prepared by essentially the same procedure except that after 2 hours of reaction, the mixture was cooled to room temperature and left to stand. After one week at room temperature, dark-green crystals formed. Anal; calcd: C, 36.7; N, 6.6; H, 5.2%. Found: C, 37.3; N, 6.7; N, 5.3%.

Measurements

The Raman spectra were obtained using a Jarrel-Ash 25–300 double monochromator Raman spectrometer fitted with a photon counting detection system. The spectra were excited with several Ar^+ and Kr^+ laser lines and resolution was about 7 cm^{-1}. The Raman spectra of compounds **I** and **II** were obtained with the samples diluted in KBr (1:40 by mass) using a rotatory disc to avoid thermal decomposition. Compound **I**, a very poor Raman scatterer and sensitive to laser radiation, when excited far from the resonance condition (*ca* 517 nm) shows a Raman spectrum with very low signal/noise ratio. Resonance Raman spectra were obtained with the sample diluted in Na_2SO_4 (1:100 by mass), which was used as an internal standard, using again a rotatory disc. The resonance Raman profiles were made using the sulfate band at *ca* 990 cm^{-1} as internal standard (I_{Raman}/I_{990}). The IR espectra were obtained with a Perkin-Elmer 180 spectrometer and the electronic spectra were obtained with a Hitachi UV-VIS-NIR spectrophotometer.

RESULTS AND DISCUSSION

The electronic spectra of **I** and **II** in acetonitrile are shown in Figure 2(a,b). Raman and IR spectra are shown in Figures 3(a,b) and 4(a,b), respectively. Table 1 lists Raman and IR frequencies for **I** and **II**, together with a tentative assignment. As can be seen in Figure 2a, **I** presents bands at 240, 318, 369 and 517 nm, while **II** shows bands at 225, 245, 323, 390 and 1408 nm. The rather intense bands at *ca* 230, and 225, 245 nm, for **I** and **II**, respectively, can be easily assigned to internal transitions

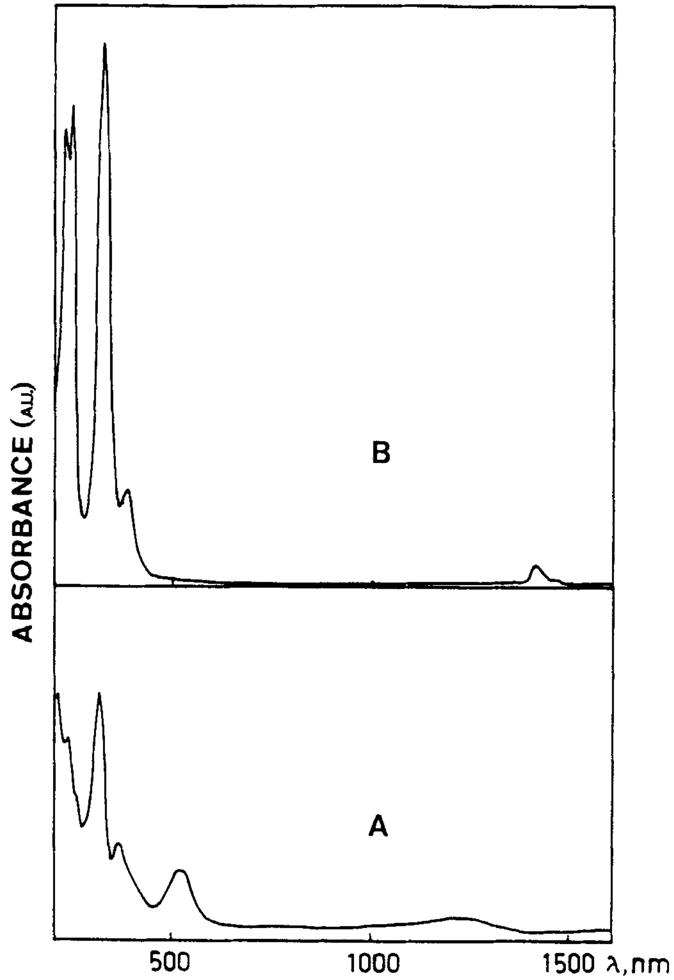

Figure 2 Electronic spectra of (a) $[Ni(dmit)_2(piperidine)_2]^-$ (2×10^{-5} M) in acetonitrile, (b) $[Ni(dmit)(piperidine)_2]$ (10^{-5} M) in acetonitrile.

of piperidine and the weak band at 1408 nm can be assigned to a Ni^{2+} d-d transition.

The remaining bands can then be assigned to internal transitions of dmit or to charge transfer transitions. In the case of **II**, the so-called interligand transition is very unlikely since piperidine does not have available molecular orbitals at sufficiently low energy and with the correct symmetry to participate in the extended π system, as is the case for species featuring two dmit ligands in their structures. One of the most striking differences in the electronic spectra of **I** and **II** is the presence of a rather intense band at 517 nm ($\varepsilon = 5.8 \times 10^3\ M^{-1}\ cm^{-1}$), present in

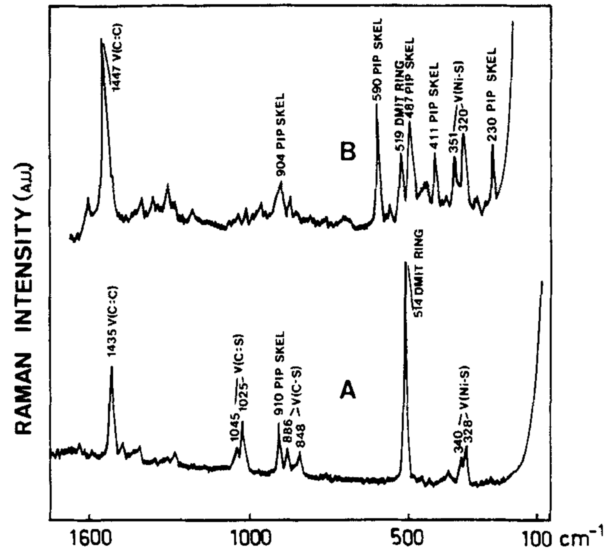

Figure 3 Raman spectra in a KBr mixture (1:40 by mass) using rotatory disc for (a) $[Ni(dmit)_2(piperidine)_2][NBu_4]$ with 514.5 nm excitation, (b) $[Ni(dmit)(piperidine)_2]$ with 647.1 nm excitation.

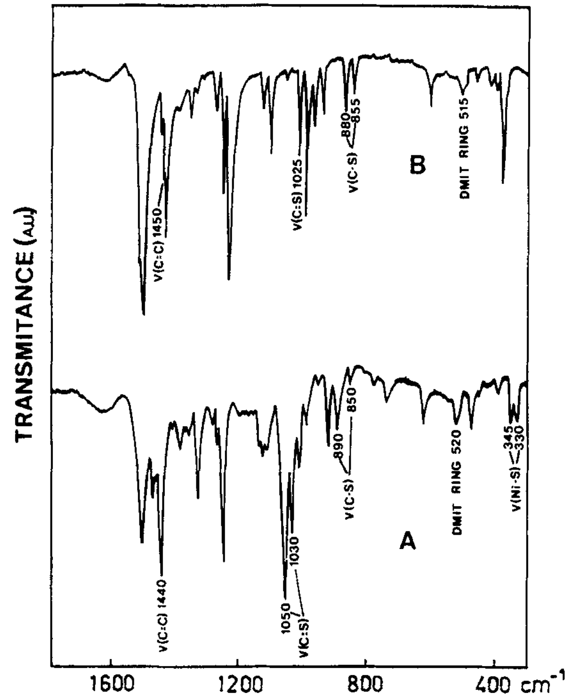

Figure 4 IR spectra in KBr pellets of (a) $[Ni(dmit)_2(piperidine)_2][NBu_4]$, (b) $[Ni(dmit)(piperidine)_2]$.

Table 1 IR wavenumbers (cm^{-1}) and Raman shift (cm^{-1}) in the solid state and a tentative assignment for [Ni(dmit)$_2$(piperidine)$_2$]$^-$ and [Ni(dmit)(piperidine)$_2$].

[Ni(dmit)$_2$(pip)$_2$]$^-$		[Ni(dmit)(pip)$_2$]		Assignment*
IR	Raman	IR	Raman	
	248vw		230m	pip skel def
			280w	pip skel def
330m	328s		320m	ν(Ni-S)
345m	340m		351m	ν(Ni-S)
390w	380w	390s	370w	pip skel def
	403vw	405w	411m	pip skel def
445w	442vw	425w	437w	dmit ring + ν(Ni-S)
470m	465vw	480w	487m	pip skel def
520m	514vs	515w	519m	dmit ring breath
			556w	
			590s	pip skel puls
620m		615m		pip skel def
740m				
780w				pip skel def
850w	848m	855m	852w	dmit ν(C-S)
890m	886m	880m	872w	dmit ν(C-S)
915m	910s		904m	pip skel stretch
950w		950m		
985m	985vw	980m	970w	p(CH$_2$)$_2$
1010m		1000s	1010w	skel stretch
1030s	1025s	1025m	1035w	dmit ν(C = S)
1050vs	1045m			dmit ν(C = S)
1110m		1110m		pip skel stretch
1120m				
1135m	1150w	1135m	1130vw	pip skel stretch
	1178vw		1178w	pip p(CH$_2$)$_2$
1240vs	1238w	1240vs	1230vw	pip p(CH$_2$)$_2$
1265w	1259vw	1260s	1253w	pip p(CH$_2$)$_2$
1280w	1280m	1285m	1295w	pip p(CH$_2$)$_2$
1325s		1340w	1337w	pip p(CH$_2$)$_2$
1350w	1346w	1360m	1355vw	pip p(N-R)
1385m				
	1402w	1400w		
		1440s	1425sh	pip r(HCH)
1440vs	1435vs	1450sh	1447vs	dmit ν(C = C)
1470m		1455sh		pip r(HCH)
1505s	1497vw	1510vs	1504w	pip r(HCH)

* Pip = Piperidine, skel def = skeletal deformation vibration, skel str = skeletal stretching vibration, skel puls = pulsed skeletal vibration, r = internal deformation vibration, p = external deformation vibration, s = strong, ve = very strong, m = medium, w = weak, vw = very weak, sh = shoulder; assignments based on refs. 4, 7, 9, 10.

the former but absent in the latter. Consequently, the band at 517 nm cannot be sensibly assigned to an internal transition of dmit, as previously suggested for [M(dmit)$_2$]$^{2-}$ species,[3] since in that case it should be also present in the spectrum of **II**. It seems then reasonable to assign the band at 517 nm to an interligand transition involving both dmit ligands.

Due to the extensive delocalization of the molecular orbitals involved, the participation of the metal ion orbitals is to be expected, as was demonstrated in the case of [Ni(dmit)$_2$]$^{2-}$.[5] The resonance Raman profile obtained close to the 517 nm band, shown in Figure 5, seems to demonstrate this point very clearly, since the

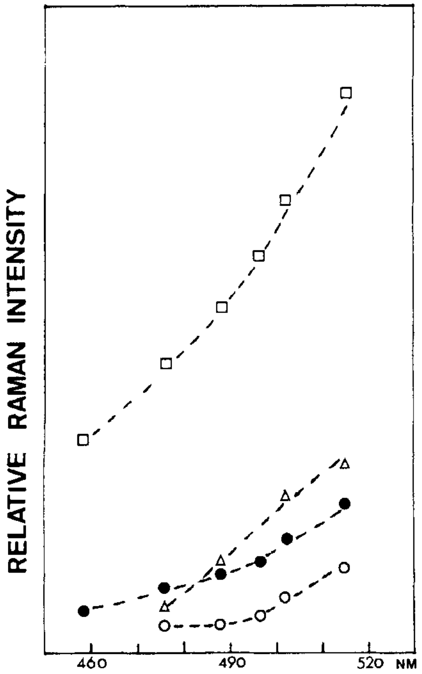

Figure 5 Resonance Raman profile of $[Ni(dmit)_2(piperidine)_2[NBu_4]$ in 1:100 (by mass) Na_2SO_4 mixture using a rotatory disc with exciting radiation (a) 514.5 nm, (b) 501.7 nm, (c) 496.5 nm, (d) 488.0 nm (e) 476 nm (f) 457.9 nm, and where (•) ν(M-S) = 328 cm^{-1}, (x) ν(thione ring) = 514 cm^{-1}, (○) ν(C = S) = 1025 cm^{-1} and (Δ) ν(C = C) = 1435 cm^{-1}. The sulfate band at *ca* 990 cm^{-1} was used as internal standard (I_{Raman}/I_{990}).

modes preferentially enhanced are related to the metal-dmit moiety, *i.e.*, 328 cm^{-1} ν(Ni-S); 514 cm^{-1} ν(thione ring); 848 cm^{-1} ν(C-S); 1025 cm^{-1} ν(C = S) and 1435 cm^{-1} ν(C = C). Previous assignments of metal-dithiolenes were made by Nakamoto and Schlapfer,[7] as well as by Clark and Turtle.[8] Specifically for $[M(dmit)_2]^-$, previous assignments wer made by Valade *et al.*,[4] as well as by Dyer *et al.*[9] Previous considerations based on the electronic spectra of **I** and **II** permit us to conclude that the intense band at 517 nm is of a charge transfer, interligand nature.

The remaining bands at 318 and 323 nm in **I** and **II** can be assigned to internal dmit transitions since they are observed in all complexes of dmit, irrespective of whether one or two dmit ligands are present. Finally, the band at 369 nm (**I**) or 390 nm (**II**) can be tentatively assigned to a charge transfer transition involving the metal ion and piperidine.

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