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Assignment of the Lowest Energy Absorption Band of Pt-bis(N,N'-di-isobutyl-dithio-oxamide) with the Use of the Resonance Raman Effect

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During the last few years interesting results have been obtained from resonance Raman (r.R.) spectra about the character of electronic transitions and about the properties of the excited states of transition metal complexes [1–3]. With the use of this r.R. effect, different electronic transitions within an absorption band could be detected and assigned. These results prompted us to investigate the electronic transitions of a representative complex of the class of metal bisdithio-oxamide compounds, which have been the subject of study for several years in our laboratories [4, 5]. Both the Pd– and Pt–bisdithio-oxamide complexes are characterized by a MS_4 coordination, having the molecular structure shown in Fig. 1 [6]. For the complex under study M = Pt, while for solubility reasons R and R' were iso-butyl groups.

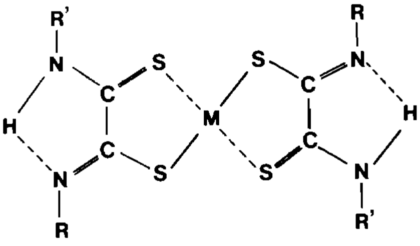

Fig. 1. Structure of one of the isomeric forms of $M(R,R'\text{-dithio-oxamide})_2$ (M = Pd or Pt).

Experimental

The complex Pt–bis(N,N'-di-isobutyl-dithio-oxamide) (I) was prepared according to the method described for the corresponding Pd-complex [5]. R.R. spectra were measured for a CH_2Cl_2 solution of complex I and recorded on a Jobin-Yvon HG2S spectrometer. The spectra were excited by a SP model 171 Ar^+ ion laser and a CR 490 tunable dye-laser with stilbene-3 as a dye. The intensities were corrected for the spectral response of the Raman spectrophotometer.

Electronic absorption spectra were recorded on a Cary 14 spectrophotometer and the m.c.d. spectra on a home-made instrument at the Laboratorium voor Algemene Chemie of the Rijksunviersiteit van Utrecht. These m.c.d. spectra were measured in $CHCl_3$ at a magnetic field strength of 7.2 tesla and they were corrected for the base-line.

Molecular orbital calculations were performed for the complex with R = R' = H according to the M.N.D.O. method described by Dewar and Thiel [7]. Interatomic distances were determined by complete geometric optimalization.

Results and Discussion

The absorption spectrum of complex I, shown in Fig. 2, possesses a strong, structured band at 450 nm which corresponds to a negative and a positive B-term in the m.c.d. spectrum at 420 and 500 nm respectively. The main electronic transition in the centre of the absorption band does not show a m.c.d. effect, although such an effect has been observed for this transition in the spectrum of the corresponding Pd-complex. Apparently the absorption band consists of at least three different electronic transitions.

The spectra show weak r.R. effects for the low frequency vibrations (300–400 cm^{-1}) but much stronger effects for Raman bands at 1192 and 1542 cm^{-1} respectively (Fig. 3). The band at 347 cm^{-1} is

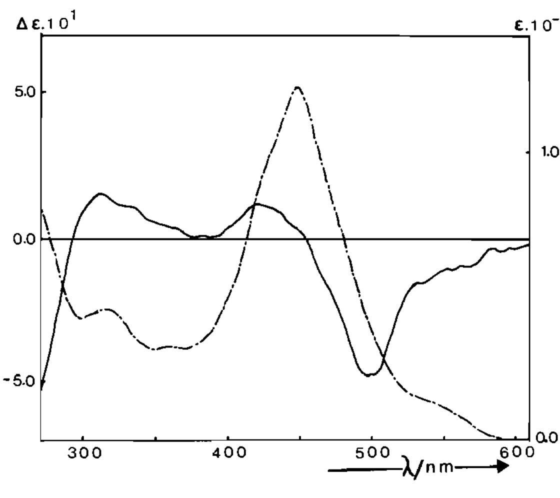

Fig. 2. Absorption (– · –) and m.c.d. (——) spectrum of complex I in $CHCl_3$.

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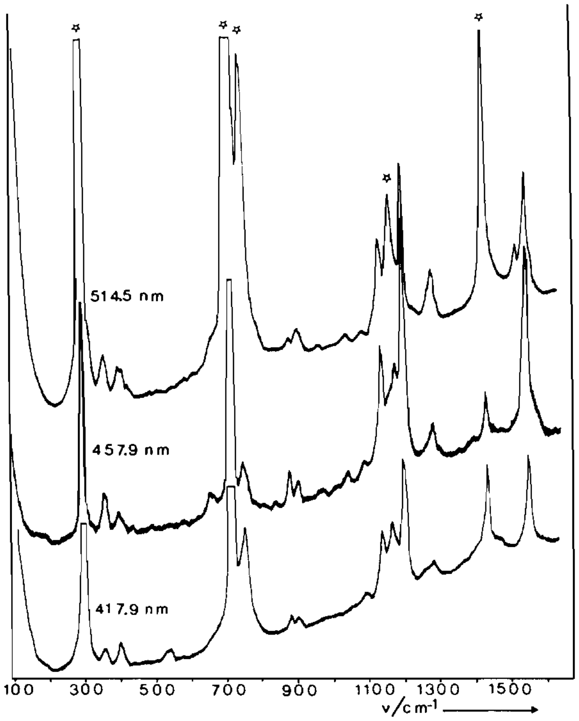

Fig. 3. Resonance Raman spectra of complex I excited with different laser lines. The bands, indicated with an asterisk, belong to the solvent CH_2Cl_2.

assigned to ν_s(Pt–S) and the bands at 1192 and 1542 cm^{-1} to symmetrical stretching modes of the dithio-oxamide ion having predominantly ν_s(CC) and ν_s(CN) character respectively [8]. Resonance Raman intensities were measured for the most pronounced bands relative to the 1423 cm^{-1} band of CH_2Cl_2, and the excitation profiles are shown in Fig. 4. These profiles possess distinct maxima at about 435 and 460 nm. Comparing the positions of these maxima with those observed in the m.c.d. spectra, we conclude that the absorption band consists of three different electronic transitions. The properties of these transitions are characterized by the r.R. spectra.

First of all, the r.R. effect of ν_s(Pt–S) at 347 cm^{-1} is very weak, which means that the metal–sulfur bonds are hardly affected during these transitions. On the other hand, the r.R. effects of the symmetric ligand stretching modes are large. These electronic transitions are therefore assigned to ligand-localized transitions. Furthermore, the changes in intensity throughout the excitation profile are similar for all resonance-enhanced Raman bands. This means that the electronic transitions have a similar character. This result is in contrast with the r.R. data of Siiman *et al.* [9] for Ni(II) dithienes, $Ni(S_2C_2R_2)_2$, which show a strong r.R. effect for the symmetric metal–ligand stretching mode, and only weak effects for the ligand modes. On the basis of these r.R. results, Siiman assigned the absorption band of these complexes in the visible region to ligand to metal charge transfer transitions.

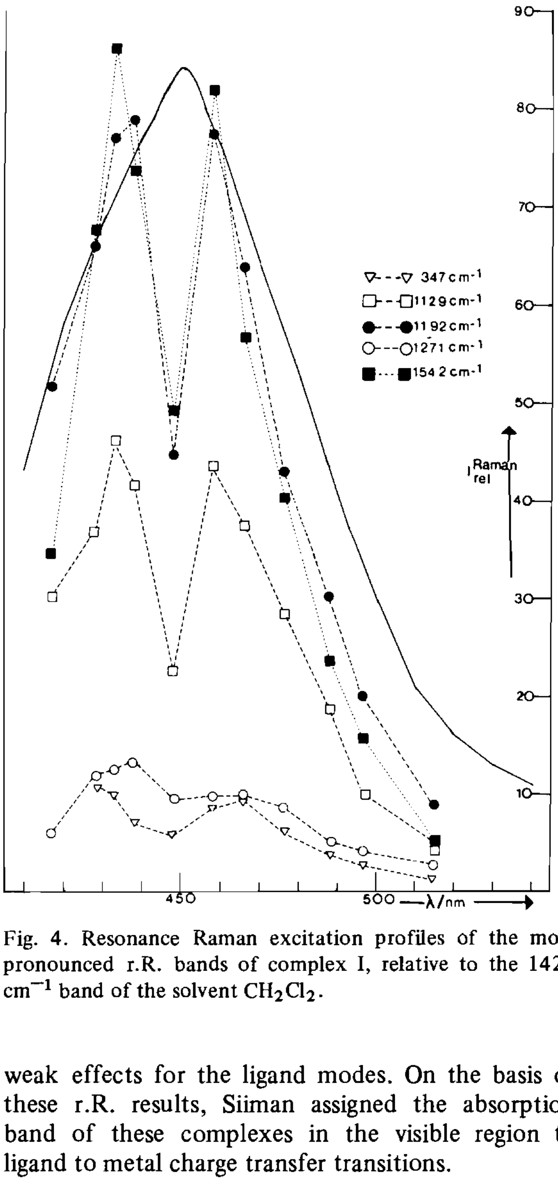

Fig. 4. Resonance Raman excitation profiles of the most pronounced r.R. bands of complex I, relative to the 1423 cm^{-1} band of the solvent CH_2Cl_2.

In order to find out whether these ligands possess such low-lying transitions, we performed a MO calculation on the dithio-oxamide ion. According to these calculations, the ion possesses as candidates for the HOMO a group of four orbitals with low ionization energy (between 4.5 and 5 eV) which nearly coincide and which have predominantly sulfur-p character (see Fig. 5). The LUMO of the ion has π^* character. Upon interaction with the Pt-d orbitals, one of the sulfur-p orbitals will be stabilized. Furthermore, in the free ion as well as in the complex, the electronic transition from this stabilized sulfur-p orbital to the LUMO is forbidden, whereas the transitions from the other three orbitals are allowed. Therefore, three low-energy transitions are expected for complex I, which are close in energy, are ligand localized, and which all have mainly

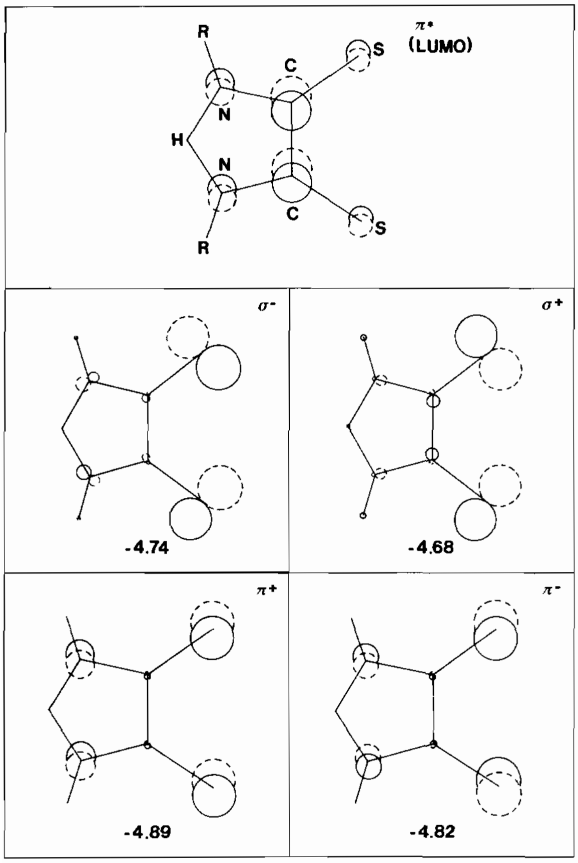

Fig. 5. Orbital plots according to [10] of the highest four occupied MOs and of the LUMO of the dithio-oxamide ion (R = R′ = H). The numbers represent the calculated orbital energies (in eV), the Greek symbols the symmetry character of the MOs.

$p_S \rightarrow \pi^*$ character. This result is in agreement with the conclusions drawn from the m.c.d. and r.R. spectra about the character and number of electronic transitions within the first absorption band of complex I.

The alternative assignment of this band to a Pt to ligand or ligand to Pt charge-transfer transition is highly improbable in view of both the r.R. and MNDO results. First of all, both kinds of transitions will invoke a strong r.R. enhancement of ν_s(Pt–S), which is not observed in the spectra. Secondly, Pt to ligand charge transfer transitions are expected at much higher energies since the Pt-d orbitals normally have a rather high ionization potential (8–9 eV) in the photoelectron spectra of Pt(II) compounds [11].

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