

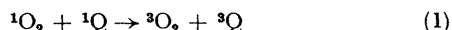
Singlet-Triplet Transitions in Square-planar Nickel Complexes which Quench Singlet Oxygen

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Summary The electronic absorption spectra in solution of four square-planar nickel(II) complexes show weak and extremely broad bands in the near i.r. region, which are assigned to singlet-triplet transitions; this is consistent with an energy-transfer mechanism for efficient quenching of singlet oxygen by these complexes.

A VARIETY of square-planar diamagnetic complexes of nickel(II) are quenchers of singlet oxygen,^{1,2} with efficiencies which not only approach that for a diffusion-controlled process, but are much higher than for paramagnetic nickel complexes of different geometry.³ However, the quenching mechanism is uncertain. One possibility is that energy transfer to give a low-lying triplet state of the complex is involved, *e.g.* equation (1).¹⁻³ A similar mechanism seems



well established for β -carotene and related conjugated dienes.^{1,4} Nevertheless, for nickel complexes, Zweig and Henderson⁵ were unable to find any correlation between the quenching efficiency and absorption at a frequency corresponding to the 0,0 band of the ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition (7880 cm^{-1} in the vapour phase, and also in $\text{CCl}_2\text{FCClF}_2$ solution⁶). The present work reports the electronic absorption spectra of four representative square-planar nickel complexes. Quenching by NN' -disalicylidene-1,2-propylenediaminatonickel(II) $[(\text{salpn})_2\text{Ni}]$ has not been reported, but the closely related, but less soluble, NN' -disalicylideneethylenediaminatonickel(II) is an efficient quencher, with k_Q *ca.* $5 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$.¹

One difficulty in measuring weak electronic bands in the near i.r. is the presence of vibrational overtone and combination bands. The weak and comparatively sharp bands

around 8500 cm^{-1} reported in the reflectance spectra of solid bis(salicylaldehyde oximato)nickel(II) and bis(*N*-methylsalicylideneaminato)nickel(II),⁷ and assigned to singlet-triplet transitions, probably arise in this way. This difficulty was largely overcome for bis(dimethyldithiophosphato)nickel(II) by deuteration of the ligand, and for bis(di-*n*-butyldithiocarbamato)nickel(II) by placing an equal concentration of bis(di-*n*-butyldithiocarbamato)zinc in the reference cell.

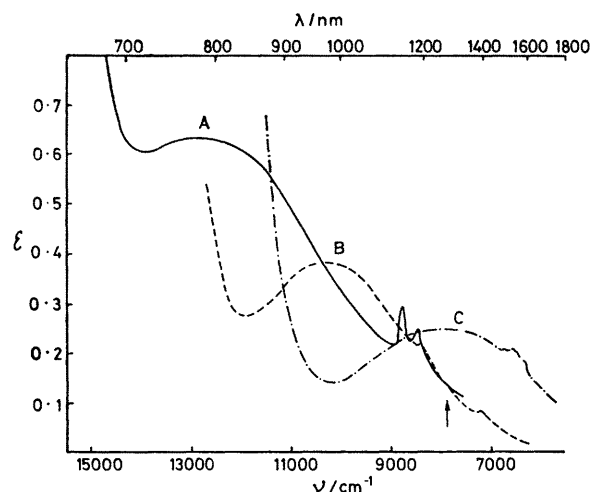


FIGURE. Absorption spectra of (A) $(\text{salpn})_2\text{Ni}$ in CDCl_3 ; (B) $(\text{Bu}_4\text{NCS}_2)_2\text{Ni}$ in CCl_4 , reference $(\text{Bu}_4\text{NCS}_2)_2\text{Zn}$; (C) $[(\text{CD}_3\text{O})_2\text{PS}_2]_2\text{Ni}$ in CCl_4 . The arrow indicates the position of the 0,0 band for the ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition.

In all cases, broad weak bands were observed in the near i.r., and three of these are shown in the Figure. These bands can be assigned to singlet-triplet transitions (probably $^3B_{1g} \leftarrow ^1A_g$ in D_{2h} symmetry).^{8,9} The absorption maxima are given in the Table, together with those for the spin-allowed d-d transitions. Except for bis(dimethyldithiophosphato)nickel(II), the singlet-triplet maxima lie well

above the energy of $^1\Delta_g$ oxygen. However, the bands are extremely broad, and even for $(\text{salpn})_2\text{Ni}$ there is still some absorption intensity at 7880 cm^{-1} . It seems likely that there is a considerable change in molecular dimensions in going to the triplet state, and that, in all cases, the 0,0 band has a value $\leq ca. 8000\text{ cm}^{-1}$. An approximate Franck-Condon analysis¹⁰ of the spectrum (vibrational envelope) of bis(di-n-butyldithiocarbamato)nickel(II) is consistent with this. A further factor involved in the high quenching efficiency of square-planar nickel(II) complexes may be their geometry, which allows a close approach of the singlet oxygen molecule to the nickel ion, with consequent efficient energy transfer.^{2,9}

Absorption spectra were measured on a Cary 14R spectrophotometer, using 5 cm quartz cells, and 0.1–0.3M solutions of the complexes.

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TABLE. Absorption maxima for d-d transitions of square-planar nickel(II) complexes. Solvent CCl_4 unless otherwise stated.

Compound	$\nu_{\text{max}}/\text{cm}^{-1}$
$(\text{salpn})_2\text{Ni}$	12,600 (CDCl_3) 18,500
$(\text{Pr}^i\text{OCS}_2)_2\text{Ni}$	10,300 15,600
$(\text{Bu}^n_2\text{NCS}_2)_2\text{Ni}$	10,260 15,650
$[(\text{CD}_3\text{O})_2\text{PS}_2]_2\text{Ni}$	20,600 (infl.) 7,870 14,490 19,030

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