Studies on Singlet Oxygen in Aqueous Solution. Part 2.[1] Water-soluble Square-planar Nickel Complexes as Quenchers

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Three water-soluble square-planar nickel complexes have been investigated as quenchers of $^1O_2$ in aqueous solution, using anthracene-9,10-bis(ethanesulphonate) as a trap. Disodium [*NN'*-ethylenebis(5-sulphosalicylideneiminato)]nickelate(II) and its propylene analogue are efficient quenchers, with $k_Q = 1.6 \times 10^9$ and 1.3×10^9 dm^3 mol^{-1} s^{-1} respectively. The value of k_Q for disodium [*NN'*-*o*-phenylenebis(5-sulphosalicylideneiminato)]nickelate(II) is much less, and seems to be concentration-dependent. This is attributed to aggregation, in agreement with the electronic and ^{1}H n.m.r. spectra.

In the study of systems where singlet oxygen may be involved, quenchers of $^1O_2$ can be useful diagnostic tools. For aqueous solutions, the two most commonly used quenchers are the N_3^- ion and 1,4-diazabicyclo[2.2.2]octane. The N_3^- ion is a reasonably efficient quencher ($k_Q = 2.2 \times 10^8$ dm^3 mol^{-1} s^{-1} in CH_3OH solution[2]), but is not always chemically inert,[3] while 1,4-diazabicyclo[2.2.2]octane is comparatively inefficient (k_Q *ca.* 2.4×10^7 dm^3 mol^{-1} s^{-1} [4]). Square-planar nickel complexes comprise a well known class of organic-soluble quenchers, some of which quench $^1O_2$ at rates approaching that for a diffusion-controlled reaction.[4-6] The quenching mechanism involves a spin-allowed energy transfer to produce a low-lying triplet level of the complex.[7]

The present work describes some water-soluble quadridentate Schiff-base complexes of this type, produced by condensation of the useful starting material salicylaldehyde-5-sulphonate (sals) with diamines in the presence of Ni^{2+}. The quenching efficiencies of these complexes were obtained using anthracene-9,10-bis(ethanesulphonate) (aes)[1] as a trap for $^1O_2$ in aqueous solution. One complex (prepared by a slightly different route) has previously been reported,[8] but does not seem to be the same as that described here. Recently, Berry *et al.*[9] used sals to prepare a variety of water-soluble Schiff-base complexes of Co^{II} and Co^{III}.

Results and Discussion

The complexes studied were (**1**)—(**4**). Complex (**1**) is soluble in water to the extent of about 5×10^{-3} mol dm^{-3}, and the other complexes are more soluble. Complex (**1**) is stable in solution over the range pH 3—12, and is unaffected by H_2O_2, $^1O_2$, and, over a period of several hours, ethylenediaminetetra-acetate (edta) (pH = 8). It is, however, fairly rapidly attacked by OCl^- and CN^-. The other complexes behave in a similar manner, although (**2**) is even slower to react with edta and (**3**) is stable to OCl^- for a few minutes. They are all diamagnetic in the solid state. In D_2O solution, complexes (**1**) and (**2**) give sharp proton resonances which have 'normal' chemical shifts (see Experimental section). The electronic spectrum of (**1**) in water is similar to those of the corresponding unsulphonated complexes in organic solvents,[10] with the lowest-energy *d-d* transition occurring at *ca.* 525 nm (ε *ca.* 100 dm^3 mol^{-1} cm^{-1}). It is therefore surprising that Mukherjee and Ray,[8] who prepared an adduct analysing as (**1**) by refluxing the Schiff base with nickel acetate, reported it to be paramagnetic with μ = 2.99 B.M. (*ca.* 2.77×10^{-23} A m^2), *i.e.* high-spin Ni^{II}.

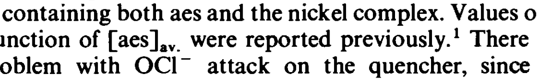
If $^1O_2$ is produced in the presence of a trap A such as aes and also a quencher Q, then in addition to reaction with A, quenching by A, and quenching by the solvent, we have reaction

$$^1O_2 + Q \xrightarrow{k_Q} {}^3O_2 + Q \qquad (1)$$

$$\frac{k_Q}{k_r} = \left(\frac{1}{E} - \frac{1}{E_0}\right)\frac{[A]_{av.}}{[Q]} \qquad (2)$$

(1). Hence we obtain expression (2) where k_r is the rate of reaction of $^1O_2$ with A, E is the fraction of $^1O_2$ which is trapped in the presence of the quencher, E_0 is the fraction that would have been trapped in the absence of the quencher, and $[A]_{av.} = (A_0 - A_\infty)/\log_e(A_0/A_\infty)$, where A_0 is the initial concentration of A and A_∞ is the final concentration. In practice, a known amount of $^1O_2$ was generated by adding OCl^- to excess of H_2O_2 containing both aes and the nickel complex. Values of E_0 as a function of $[aes]_{av.}$ were reported previously.[1] There was no problem with OCl^- attack on the quencher, since the reaction between OCl^- and H_2O_2 is very fast. The results obtained for complexes (**1**)—(**3**) are given in Table 1.

The results for complexes (**1**) and (**2**) at different concentrations are in reasonable agreement and, assuming $k_r = 4.7 \times 10^7$ dm^3 mol^{-1} s^{-1},[1] give values for k_Q of 1.6×10^9 and 1.3×10^9 dm^3 mol^{-1} s^{-1} respectively. They are clearly efficient quenchers of $^1O_2$ and the value for (**1**) is of the same order as that reported for the corresponding unsulphonated complex in toluene (3.4×10^9 dm^3 mol^{-1} s^{-1}).[5] Complex (**3**) on the other hand is a much less efficient quencher. This could be due to a slightly higher energy for the lowest triplet level, although the unsulphonated analogue of (**3**) in toluene is an efficient quencher ($k_Q = 3.7 \times 10^9$ dm^3 mol^{-1} s^{-1}).[5] Another possibility is aggregation of the anion of (**3**), which will be rigorously planar as a result of the bridging phenylene group. Aggregation in solution to form dimers or oligomers is well established for porphyrins and metalloporphyrins,[11] and is particularly marked for tetrakis(4-sulphophenyl)porphyrin and its metal complexes in aqueous solution.[12] Aggregation would also



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(**1**) CH_2CH_2
(**2**) CH_2CHCH_3
(**3**) C_6H_4
(**4**) $C_6H_3CH_3$

Table 1. Quenching of $^1O_2$ by nickel complexes

10^4[Q]	10^3[aes]$_{av.}$	Δ(aes)	$^1O_2$ produced	$1/E$	$1/E_0$	k_Q/k_r
mol dm^{-3}		μmol				
Complex (**1**)						
1.5	3.61	4.32	18.9	4.38	2.83	37.2
2	3.67	4.03	18.9	4.70	2.81	34.7
3	3.78	3.58	18.9	5.29	2.77	31.7
4	4.00	2.49	15.12	6.07	2.69	33.8
6	4.01	2.42	18.9	7.83	2.69	34.4
8	4.08	2.03	19.0	9.35	2.66	34.1
12	4.19	1.30_6	15.12	11.58	2.63	31.2
					Av.	33.9
Complex (**2**)						
4	3.85	3.37	19.0	5.65	2.74	28.0
12	4.07	1.76_4	19.0	10.78	2.66	27.5
Complex (**3**)						
3	3.45	3.13	12.0	3.84	2.90	10.8
4	3.42	3.27	13.6	4.16	2.92	10.6
4	3.70	3.85	15.2	3.94	2.80	10.6
5.5	3.40	3.29	14.85	4.52	2.92	9.8
7	3.45	3.30	15.7	4.76	2.90	9.2
8	3.77	3.32	15.2	4.57	2.77	8.5
12	3.87	2.90	15.1	5.21	2.74	7.9

Table 2. Proton chemical shifts (δ) of complex (**3**) in D_2O as a function of concentration and temperature.

	0.0016 mol dm^{-3}		0.007 mol dm^{-3}	
Resonance	298 K	343 K	298 K	343 K
CH=N	8.34[a]	8.68[b]	7.94[c]	8.21[d]
H^6	7.54	7.71	7.43	7.59
H^4	6.98	7.12	6.89	7.01
H^3	6.56	6.72	6.45	6.60
o-Phenylene	7.4_3	7.5_8	7.3_4	7.4_7

[a] Linewidth 42 Hz. [b] Linewidth 8 Hz. [c] Linewidth 12.4 Hz. [d] Linewidth 3.7 Hz.

explain the apparent tendency for k_Q to decrease with increasing concentration of complex (**3**) (Table 1), and is strongly supported by the u.v.–visible and proton resonance spectra in aqueous solution. Complexes (**1**) and (**2**) obeyed Beer's law over the range (0.04—2) × 10^{-3} mol dm^{-3}, but for (**3**) the absorption coefficient of the band at 445 nm fell by *ca.* 15% over the range (0.02—1) × 10^{-3} mol dm^{-3}. The proton resonance spectra of complex (**3**) show marked temperature and concentration effects (Table 2). As the temperature is lowered or the concentration is increased, the proton resonances shift to high field, as expected from long-range shielding effects in an aromatic 'stacked' dimer or oligomer.

Broadening of the resonances also occurs. This is particularly marked for the CH=N resonance, and the corresponding linewidths (widths at half-height) are also given in Table 2. One possible explanation is that exchange between the dimer (oligomer) and the monomer is not completely fast on the n.m.r. time-scale, a factor which would be accentuated by the high operating frequency of the spectrometer used (250 MHz). The sharpening of the resonances at the higher temperature, and the fact that the broadening is greatest for the CH=N proton which shows the largest changes in δ, are both consistent with this interpretation. The resonances are sharper in the more concentrated solution (0.007 mol dm^{-3}), which would imply that here the dimer is the predominant species. The exchange broadening Δ in the intermediate-to-fast exchange region is given[13] by the expression $\pi\Delta = p_A{}^2 p_B{}^2 (\omega_A - \omega_B)^2(\tau_A + \tau_B)$, where p_A and p_B are the respective populations of sites A and B, ω_A and ω_B are the resonance frequencies, and τ_A and τ_B are the lifetimes. An alternative explanation of the n.m.r. data is that a small amount of a paramagnetic complex is formed by axial coordination of two H_2O molecules. However, at the high dilutions used here no concentration effect would be expected, and also it is unlikely that in such a situation all the resonances would shift in the same direction.

The electronic spectrum of complex (**4**) in aqueous solution is very similar to that of (**3**). Over the concentration range (0.02—1) × 10^{-3} mol dm^{-3}, the absorption coefficient of the band at 445 nm decreased by *ca.* 17%. It seems clear that aggregation is also occurring in this system, and it was not investigated further.

Experimental

Sodium Salicylaldehyde-5-sulphonate Monohydrate (*sals*).—*N*-Phenylsalicylideneimine-5-sulphonic acid[9] (25 g) in an aqueous solution of Na_2CO_3 (13.8 g in 125 cm^3) was boiled vigorously in an open flask for 2—2.5 h, with periodic replenishment of the evaporated water. Glacial acetic acid was slowly added to the cooled solution (100 cm^3) to a pH of *ca.* 5, followed by an equal volume of ethanol. The mixture was cooled to 0 °C, the solid filtered off, washed well with ethanol, and air-dried. Yield 10.7 g (Found: C, 34.65; H, 2.85. $C_7H_7NaO_6S$ requires C, 34.7; H, 2.90%).

Complex (**1**).—To a solution of sals (0.48 g, 0.002 mol) in water (10 cm^3) was added ethylenediamine (74 μl, 0.0011 mol), followed by $Ni(ClO_4)_2 \cdot 6H_2O$ (0.42 g, 0.00115 mol). 1 mol dm^{-3} Sodium hydroxide was then added to pH *ca.* 8. The mixture was stored overnight, and ethanol (5 cm^3) added. The orange solid was filtered off, washed with ethanol–water (1:1) followed by ethanol, and air-dried. Yield 0.35 g (56%) (Found: C, 33.9; H, 2.40; N, 4.80. $C_{16}H_{16}Na_2NiO_{10}S_2$ requires C, 34.0; H, 2.85; N, 4.95%). U.v.–visible in water: 525 (*ca.* 100), 386 (4 800), 370 (3 200), *ca.* 322 (7 800), 307 (8 000), 272 (18 800), and 249 nm (ε 66 300 dm^3 mol^{-1} cm^{-1}). ^{1}H N.m.r. (D_2O): δ 3.43 (4 H, s, CH_2CH_2), 6.88 (2 H, d, H^3), 7.54 (2 H, dd, H^4), 7.75 (2 H, d, H^6), and 7.92 (2 H, s, CH=N); $J_o{}^H$ 8.92, $J_m{}^H$ 2.36 Hz.

Complex (**2**).—This was prepared as for (**1**), substituting 1,2-diaminopropane (94 μl, 0.0011 mol) for the ethylenediamine. Yield 0.42 g (66%) (Found: C, 35.6; H, 2.80; N, 4.65. $C_{17}H_{18}N_2Na_2NiO_{10}S_2$ requires C, 35.25; H, 3.15; N, 4.85%). ^{1}H N.m.r. (D_2O): δ 1.38 (3 H, d, CH_3), 3.05 (1 H, m, C*H*CH_2), 3.5 (2 H, m, CH_2), 6.86 (1 H, d, H^3), 6.89 (1 H, d, $H^{3'}$), 7.51 (1 H, dd, H^4), 7.55 (1 H, dd, $H^{4'}$), 7.73 (1 H, d, H^6), and 7.77 (1 H, d, $H^{6'}$). Because of the asymmetric bridge, the protons of each ring are no longer equivalent.

Complex (**3**).—To a solution of sals (0.48 g, 0.002 mol) and 1,2-diaminobenzene (0.12 g, 0.0011 mol, recrystallized four times from water in the presence of decolourizing charcoal) in water (10 cm^3) was added $Ni(ClO_4)_2 \cdot 6H_2O$ (0.42 g, 0.00155 mol) and $NaO_2CMe \cdot 3H_2O$ (0.4 g, *ca.* 0.003 mol) in water (5 cm^3). The solution was heated to boiling, and ethanol (*ca.* 25 cm^3) added *via* the condenser. A mass of orange solid precipitated. The mixture was refluxed overnight, and cooled to room temperature. The solid was filtered off, washed with ethanol–water (3:1) followed by ethanol, and air-dried. Yield 0.50 g (74%) (Found: C, 39.15; H, 2.60; N, 4.55. $C_{20}H_{16}N_2Na_2NiO_{10}S_2$ requires C, 39.2; H, 2.65; N, 4.55%).

Complex (**4**).— This was prepared as for (**3**), substituting recrystallized 3,4-diaminotoluene (0.13 g, 0.0011 mol) for the 1,2-diaminobenzene. Yield 0.55 g (80%) (Found: C, 39.65; H, 2.80, N, 4.45. $C_{21}H_{18}N_2Na_2NiO_{10}S_2$ requires C, 40.2; H, 2.90; N, 4.45%).

In all cases the weight loss on heating was consistent with the presence of two H_2O molecules.

Measurements of quenching efficiency were made using the caesium salt of anthracene-9,10-bis(ethanesulphonate) (aes) as a trap for $^1O_2$ in the manner described previously,[1] except for the presence of various concentrations of the nickel complexes. The disappearance of aes was normally followed using the u.v. maximum at 398 nm. The (small) absorbances of the complexes at this wavelength were compensated by placing an aqueous solution containing an equal concentration in the reference cell. Electronic spectra were recorded on a Perkin-Elmer 551 spectrometer, and ^1H n.m.r. spectra at 250 MHz on a Bruker WM-250 FT spectrometer.

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