Some Water-soluble Schiff-base Complexes of Nickel(II): The Role of Water†

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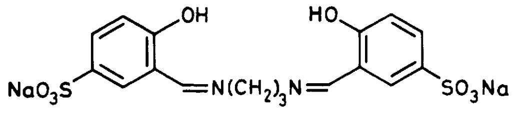
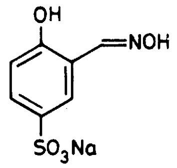
Disodium [*NN'*-propane-1,3-diylbis(salicylideneimine-5'-sulphonato)(4−)]nickelate(II), $Na_2[Ni(salpds)]$, and disodium bis[salicylaldoxime-5-sulphonato(2−)]nickelate(II) have been prepared. Electronic spectra and magnetic susceptibility measurements show that in aqueous solution there is an equilibrium between the square-planar forms and six-co-ordinate species produced by co-ordination of two water molecules. Thermodynamic parameters are reported for the $Na_2[Ni(salpds)]$ system. The room-temperature i.r. spectrum of solid (diamagnetic) $Na_2[Ni(salpds)]\cdot 2H_2O$ gives two well resolved bands in the O–H stretching region. One of these is extremely sharp (bandwidth 16 cm^{-1}) and occurs at an unusually high frequency (3 630 cm^{-1}). The i.r. spectra of samples having various extents of deuteriation show that the two water molecules are crystallographically equivalent, with C_1 site symmetry. In each H_2O, one hydrogen atom is almost non-hydrogen-bonded while the other is involved in a hydrogen bond of moderate strength.

A previous paper[1] described some water-soluble square-planar complexes of Ni^{II} with Schiff bases, obtained by condensation of sodium salicylaldehyde-5-sulphonate (sals) with 1,2-diamines in the presence of Ni^{2+}. These complexes, which were mainly of interest as quenchers of $^1O_2$, were square planar both in the solid state and in aqueous solution. The present work is concerned with two related complexes, disodium [*NN'*-propane-1,3-diylbis(salicylideneimine-5'-sulphonato)(4−)]nickelate(II), $Na_2[Ni(salpds)]$, and disodium bis[salicylaldoxime-5-sulphonato(2−)]nickelate(II), $Na_2[Ni(saldoxs)_2]$, which behave in a different manner.



$Na_2(H_2salpds)$



Na(Hsaldoxs)

Experimental

Sodium salicylaldehyde-5-sulphonate (sals) was prepared as described previously.[1]

$Na_2[Ni(salpds)]\cdot 2H_2O$.—To sals (0.48 g, 0.002 mol) in water (5 cm^3) was added 1,3-diaminopropane (92 μl, 0.0011 mol), followed by a strong aqueous solution of $NiCl_2\cdot 6H_2O$ (0.26 g, 0.0011 mol) and $Na(O_2CMe)\cdot 3H_2O$ (0.4 g, 0.003 mol). Ethanol (*ca.* 30 cm^3) was slowly added, and the mixture stirred for 12 h, over which time the initial green-brown precipitate became dark brown. The solid was filtered off, washed with aqueous ethanol (anhydrous ethanol leads to dehydration), and air-dried. Yield 0.46 g (63%) (Found: C, 35.1; H, 2.55; N, 4.70. $C_{17}H_{18}N_2Na_2NiO_{10}S_2$ requires C, 35.25; H, 3.15; N, 4.85%). The green anhydrous form was prepared by heating the brown dihydrate *in vacuo* at 70 °C (Found: C, 37.5; H, 2.65; N, 5.25. $C_{17}H_{14}N_2Na_2NiO_8S_2$ requires C, 37.6; H, 2.60; N, 5.15%).

$Na_2(H_2salpds)$.—The salt sals (0.51 g, 0.0021 mol) and ethanol (75 cm^3) were stirred and heated to 60 °C. Water was added dropwise until the solid just dissolved, followed by a strong ethanolic solution of 1,3-diaminopropane (92 μl, 0.0011 mol). After 1 h the mixture was cooled to 0 °C. The solid was filtered off, washed with aqueous ethanol, ethanol, and finally diethyl ether, and air-dried. It was obtained as the monohydrate. Yield 0.16 g (30%) (Found: C, 40.15; H, 3.50; N, 5.45. $C_{17}H_8N_2Na_2O_9S_2$ requires C, 40.6; H, 3.60; N, 5.55%).

$Na_2[Ni(saldoxs)_2]$.—To sals (0.48 g, 0.002 mol) in water (5 cm^3) was added, with stirring, $NH_2OH\cdot HCl$ (0.15 g, 0.0022 mol), then $NiCl_2\cdot 6H_2O$ (0.26 g, 0.0011 mol), and finally 1 mol dm^{-3} NaOH to pH *ca.* 8. After 1 h the green solid formed was filtered off, washed with a little ice-cold water, and air-dried. Yield (anhydrous) 0.27 g (46%) (Found: C, 31.45; H, 1.85; N, 5.20. $C_{14}H_{10}N_2NaNiO_{10}S_2$ requires C, 31.45; H, 1.90; N, 5.25%).

Sodium Salicylaldoxime-5-sulphonate, Na(Hsaldoxs).—Ethanol (10 cm^3) was added to $NH_2OH\cdot HCl$ (0.32 g, 0.0045 mol) and $Na(O_2CMe)\cdot 3H_2O$ (0.62 g, 0.0045 mol) in water (1 cm^3). After cooling to 0 °C, the NaCl was filtered off and washed with a little ethanol. The filtrate was mixed with sals (1.0 g, 0.0041 mol) in water (10 cm^3). After warming for a few minutes the solvent was removed on a rotary evaporator. The residue was stirred with ethanol, and finally washed with ethanol and air-dried. Yield (anhydrous) 0.46 g (42%) (Found: C, 34.3; H, 2.45; N, 5.55. $C_7H_6NaNO_5S$ requires C, 35.15; H, 2.55; N, 5.85%). A qualitative test indicated slight contamination with NaCl. The ^1H n.m.r. (D_2O) spectrum showed that, unlike $Na_2(H_2salpds)$, there was no hydrolysis to give sals.

$Na_2[Pd(saldoxs)_2]$.—Palladium(II) chloride (0.108 g, 0.000 61 mol), NaCl (0.071 g, 0.001 22 mol), and water (5 cm^3) were stirred together for 1 h to produce a clear red solution. The salt Na(Hsaldoxs) (0.292 g, 0.001 22 mol) was added. The colour changed immediately to bright yellow, followed by precipitation of a yellow solid. After 1 h the solid was filtered off, washed with a little water, and air-dried. Yield (anhydrous) 0.28

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† *Non-S.I. unit employed:* B.M. ≈ 9.27 × 10^{-24} A m^2.

g (79%) (Found: C, 28.25; H, 1.75; N, 4.65: $C_{14}H_{10}N_2Na_2O_{10}PdS_2$ requires C, 28.65; H, 1.75; N, 4.80%); $\lambda_{max.}(H_2O)$ = 422 (ε *ca.* 83, inflection), 354 (7 220) and 282 nm (ε 10 400 $dm^3 mol^{-1} cm^{-1}$). For all compounds the degree of hydration (if any) was confirmed by heating *in vacuo* to constant weight.

Deuteriation of $Na_2[Ni(salpds)]\cdot 2H_2O$.—Dissolution of samples of the dihydrate in D_2O and drying *in vacuo* or over desiccants led to dehydration. Accordingly, $Na_2[Ni(salpds)]\cdot 2H_2O$ was dissolved in D_2O and reprecipitated with CH_3CH_2OD. The solid was centrifuged off under argon, and the mother-liquor removed by anaerobic transfer. A stream of argon was blown over the solid for a few hours to remove the remaining deuterioethanol. The solid was then placed in a desiccator over a saturated solution of $CaCl_2$ in D_2O for a few weeks. The extent of deuteriation, as indicated by the i.r. spectrum, was *ca.* 95%. The deuterium content was varied by exposure to atmospheric moisture or, for low contents, by standing over water in a desiccator.

Electronic spectra were recorded on Perkin-Elmer 551 and Pye-Unicam 108 spectrometers. For the variable-temperature measurements, an R11C cell and power supply was used, and the temperatures measured with a Comark electronic thermometer and chromel–alumel thermocouple. Infrared spectra were obtained on a Perkin-Elmer 597 spectrometer, using the narrow-slit program. Variable-temperature magnetic susceptibility measurements were made using an n.m.r. method[2,3] on a Perkin-Elmer R32 spectrometer. The Wilmad 517 coaxial n.m.r. tubes contained a buffered solution of the complex and excess of ligand in the inner tube, and buffer and ligand in the outer tube. The reference was 2% Bu^tOH.

Results and Discussion

$Na_2[Ni(salpds)]$.—Depending on the conditions, the solid complex is obtained either as a brown dihydrate or in a green anhydrous form. The dihydrate is diamagnetic, and the reflectance spectrum shows an inflection at *ca.* 495 nm. It is clear that the complex is square planar, and that the water molecules are not co-ordinated to the nickel. Their detailed nature is discussed below. The green form has a magnetic moment of *ca.* 1.4 B.M., and the reflectance spectrum shows bands at *ca.* 495 (inflection) and 610 nm. The exact nature of this form is obscure, but it is probably polymeric, containing either a mixture of high-spin (six co-ordinate) and low-spin square-planar nickel ions, or nickel ions in an intermediate spin state with weak axial co-ordination. The complex $Na_2[Ni(salpds)]$ differs considerably in behaviour from the unsulphonated species [Ni(salpd)]. The latter occurs in either an anhydrous brown diamagnetic form[4,5] or as a green paramagnetic (μ = 3.28 B.M.) dihydrate.[5,6]

The green and brown forms of $Na_2[Ni(salpds)]$ dissolve in water to give the same green solution. This solution is also formed from aqueous Ni^{2+} with either the ligand or a 2:1 molar ratio of sals and 1,3-diaminopropane over the range pH 6—9 (6—12 when the ligand : Ni ratio is 2.5:1). The green solution turns reversibly brown on heating. At 298 K bands are observed at 845 (ε 10), 745 (7), and 585 nm (14 $dm^3 mol^{-1} cm^{-1}$) and, in the absence of excess of ligand, a shoulder at *ca.* 490 nm. Beer's law was obeyed over the concentration range 0.01—0.05 mol dm^{-3}. On heating to 358 K the bands at 845 and 745 nm decrease in intensity, that at 585 nm becomes partially observed as a shoulder, and the shoulder at *ca.* 490 nm increases considerably in intensity. These changes in the long-wavelength region, where ligand absorption is negligible, are shown in Figure 1. Addition of ethanol to the green solution at room temperature produces changes similar to those caused by heating. It appears that an equilibrium exists between a square-planar species and a six-co-ordinate one produced by axial co-ordination of two water molecules [equation (1)]. The bands at

$$[Ni(salpds)]^{2-} + 2H_2O \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} [Ni(salpds)(H_2O)_2]^{2-} \quad (1)$$

845, 745, and 585 nm can be ascribed to the diaquo-species, and are characteristic of Ni^{II} in a distorted octahedral environment,[7] with the highest energy *d–d* transition obscured by absorption of the ligand, and also of the square-planar form. The latter gives rise to the shoulder at *ca.* 490 nm, which is similar to that observed in the reflectance spectrum of the solid dihydrate.

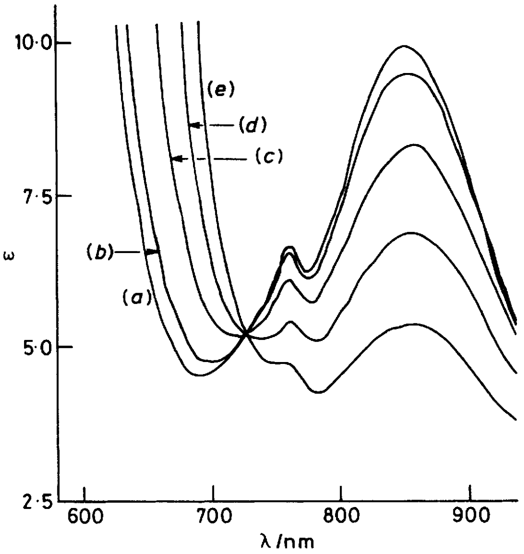

Figure 1. The electronic absorption spectra of $Na_2[Ni(salpds)]$ in aqueous solution as a function of temperature: (*a*) 274, (*b*) 294, (*c*) 323, (*d*) 343, and (*e*) 363 K. Ligand to Ni^{2+} ratio 2.5:1, pH 8 (0.2 mol dm^{-3} *N'*-2-hydroxyethylpiperazine-*N*-propanesulphonic acid buffer)

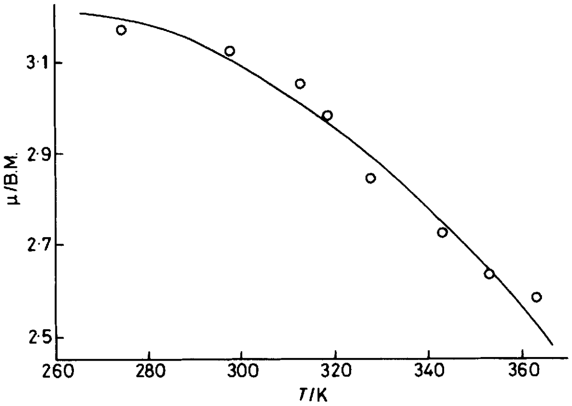

Figure 2. The magnetic moment μ of $Na_2[Ni(salpds)]$ in water (pH 8) as a function of temperature. The curve is calculated from the computer program

This interpretation was confirmed by measuring the magnetic susceptibility of the complex in solution. The magnetic moment μ fell from 3.17 B.M. at 275 K to 2.58 at 363 K (Figure 2). For an equilibrium between a diamagnetic and a paramagnetic species in solution we have equation (2), where μ is the observed

$$\log_e\left(\frac{\mu^2}{\mu_h^2 - \mu^2}\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

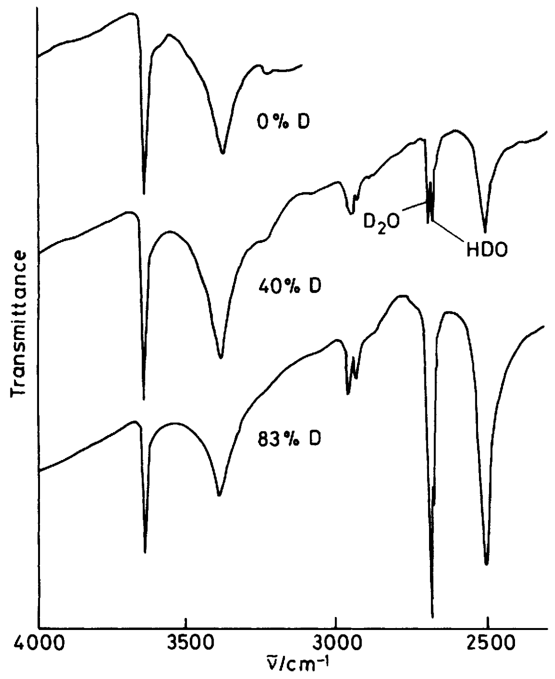

Figure 3. The i.r. spectra of $Na_2[Ni(salpds)]\cdot 2(H,D)_2O$ at various degrees of deuteriation in Voltalef 3S mulls (Nujol for the undeuteriated sample)

magnetic moment at temperature T and μ_h is the magnetic moment of the paramagnetic form. One method of treating the experimental data would be to vary the unknown μ_h until the best correlation coefficient was obtained for a plot of the left-hand side of equation (2) against $1/T$ (*cf.* ref. 3). In the present case this procedure is not entirely satisfactory. At the lowest temperatures the complex is very largely in the paramagnetic form, and accordingly these points are unduly weighted. This problem can be overcome by rearrangement of the above expression to give equation (3).

$$\mu = \mu_h/[1 + e^{(\Delta H/RT - \Delta S/R)}]^{\frac{1}{2}} \qquad (3)$$

A computer program was used to vary μ_h, ΔH, and ΔS so as to minimise $\Sigma\,(\mu^2_{calc.} - \mu^2)^2$. The values thus obtained are μ_h = 3.269 B.M., $\Delta H = 25 \pm 9$ kJ mol^{-1}, and $\Delta S = -65 \pm 25$ J K^{-1} mol^{-1}, and the curve obtained using these parameters is shown in Figure 2. A similar equilibrium has been observed for complexes of Ni^{II} with a variety of quadridentate nitrogen-containing ligands in aqueous solution,[8] and the reported values of ΔS are of the same order of magnitude as that obtained here. One can also calculate that, at 274 K, *ca.* 4% of the complex is present in the square-planar form, and at 363 K, *ca.* 39%. These figures are reasonably consistent with the changes in intensity of the electronic band at 845 nm (Figure 1). The different behaviour in aqueous solution of $Na_2[Ni(salpds)]$ and the other nickel complexes described previously,[1] which were prepared from 1,2-diamines, may be associated with the weaker in-plane bonding in the former, as a consequence of the six-membered ring.

Infrared Spectroscopic Study of the Water in $Na_2[Ni(salpds)]\cdot 2H_2O$.—The i.r. spectra of most solid hydrates show rather broad and featureless absorption in the OH-stretching region. The complex $Na_2[Ni(salpds)]\cdot 2H_2O$ is unusual in that two well defined bands are observed (Figure 3), one of them being very sharp (width 16 cm^{-1}), and at an unusually high frequency (3 630 cm^{-1}). Accordingly, the O–H and O–D stretching regions were studied for samples varying in the extent of deuteriation from 0 to 95%. At high and low degrees of deuteriation, two 'isolated' O–H or O–D stretches were observed, indicating that the complex contains only two distinct O–H (or O–D) bonds.[9,10] This could result either from two crystallographically equivalent water molecules with C_1 site symmetry, *i.e.* H^1OH^2, or two different water molecules with C_{2v} symmetry, *i.e.* H^1OH^1 and H^2OH^2. A direct distinction between these two possibilities could be made by observing the 'isolated' bending fundamentals, since the number of these is equal to the number of crystallographically distinct water molecules present.[9,10] Unfortunately, in $Na_2[Ni(salpds)]\cdot 2H_2O$ the expected region is obscured by ligand absorption. However, it is clear that the first possibility is correct. If two different water molecules were present, then, in the undeuteriated dihydrate, *four* O–H stretches, rather than two, would be expected, corresponding to ν_{sym} and ν_{asym} for each H_2O. The possibility that one band in each pair is too weak to be observed can be discarded, since the O–H stretching frequencies in the undeuteriated dihydrate are very close to the 'isolated' frequencies (Table). In water vapour the symmetric and asymmetric OH stretches are quite widely separated at 3 652 and 3 756 cm^{-1} respectively,[11] while in HDO the 'isolated' O–H stretch is at 3 707 cm^{-1},[12] close to the arithmetic mean of ν_{sym} and ν_{asym}. The frequencies and bandwidths observed for $Na_2[Ni(salpds)]\cdot 2H_2O$ and its deuteriated forms are given in the Table.

Table. Infrared wavenumbers and bandwidths at half-height (in brackets) (cm^{-1}) for $Na_2[Ni(salpds)]\cdot 2(H,D)_2O$ at room temperature. See also Figure 3

	O–H^1	O–H^2	O–D^1	O–D^2
H_2O	3 630 (16)	3 378 (109)		
HDO (dilute)	3 629 (9)	3 384 (55)	2 674 (*ca.* 4)	2 503 (28)
D_2O			2 686 (*ca.* 9)	2 497 (30)

The 'isolated' O–H stretching frequencies of 3 629 and 3 384 cm^{-1}, and the corresponding OD frequencies of 2 674 and 2 503 cm^{-1}, show clearly that one H atom (H^1) is very weakly hydrogen-bonded, if at all, while the other is involved in a hydrogen bond of moderate strength. As a result there is little intramolecular coupling, and the frequencies for the HDO molecules are close to the corresponding ones for H_2O and D_2O. The sharpness of the non-isolated OH^1 and OD^1 bands suggests that there is also very little intermolecular coupling between like vibrations in the unit cell.[10,13]

The situation in $Na_2[Ni(salpds)]\cdot 2H_2O$ is similar, in some respects, to that in $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$, which shows two quite sharp O–H stretches at 3 625 and 3 545 cm^{-1}. This molecule has been the subject of several i.r. studies, but by far the most detailed work is that of Falk and his co-workers.[10] By using the deuteriation technique at variable temperatures they confirmed an *X*-ray study,[14] which showed that the two water molecules are equivalent, with C_1 site symmetry, and are only very weakly hydrogen-bonded. The 'isolated' O–H and O–D stretching frequencies are 3 603, 3 568, 2 653.5, and 2 629.5 cm^{-1} respectively (30 °C). This suggests that, in $Na_2[Ni(salpds)]\cdot 2H_2O$, H^1 is even more weakly hydrogen-bonded than either of the two distinct H atoms in $Na[Fe(CN)_5(NO)]\cdot 2H_2O$, although O–H stretching frequencies in hydrates will be affected slightly by factors other than hydrogen bonding, such as dispersion forces and co-ordination to cations.

$Na_2[Ni(saldoxs)_2]$.—In the solid state, $Na_2[Ni(saldoxs)_2]$ is diamagnetic and the reflectance spectrum shows bands at 622

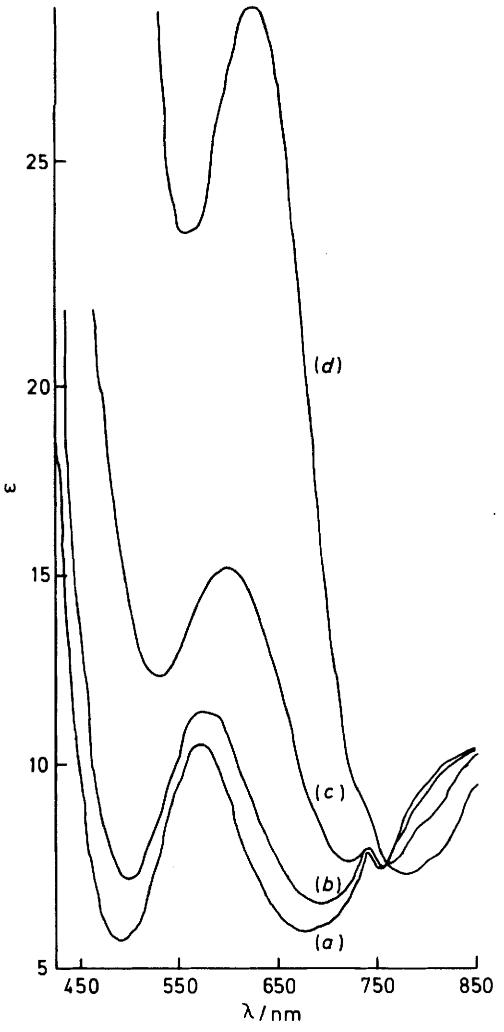

Figure 4. The electronic absorption spectra of $Na_2[Ni(saldoxs)_2]$ in aqueous solution (pH 8) as a function of temperature: (*a*) 274, (*b*) 294, (*c*) 323, and (*d*) 358 K

and *ca.* 460 nm (inflection). It is thus very similar to the well known unsulphonated analogue bis(salicylaldoximato)nickel(II), $[Ni(saldox)_2]$. The latter, which has been shown by *X*-ray crystallography to exist in a *trans*-planar form,[15] gives reflectance bands at 625 and *ca.* 470 nm (inflection) [620—625 (ε *ca.* 100 $dm^3 mol^{-1} cm^{-1}$), *ca.* 470 nm (inflection) in $CHCl_3$].[16] In aqueous solution, $Na_2[Ni(saldoxs)_2]$ behaves in a similar manner to $Na_2[Ni(salpds)]$. At 298 K bands are observed at 920 (ε 8), 740 (6), and 585 nm (9 $dm^3 mol^{-1} cm^{-1}$). On heating to 358 K the band at 585 nm increases in intensity and shifts to 619 nm. At 274 K the maximum occurs at 573 nm (Figure 4). The bands at 920, 740, and *ca.* 573 nm can be assigned to the six-coordinate species, and that at 619 nm to the square-planar form. The magnetic moment μ also falls from 3.15 to 2.87 B.M. over the range 275—358 K. These changes in μ are insufficient to permit the calculation of thermodynamic parameters as was done for the analogous $Na_2[Ni(salpds)]$ system. However, it can be estimated from the magnetic moment and the electronic absorption spectrum, at 358 K, that *ca.* 20% of the square-planar form is present.

The corresponding palladium complex $Na_2[Pd(saldoxs)_2]$ was also prepared. As expected the first *d*–*d* transition (422 nm) is at much higher energies than in $Na_2[Ni(saldoxs)_2]$ (620 nm).

Acknowledgements

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