

Spectroscopic and Electrochemical Studies on Dinuclear Mixed Ni(II)-Chelates **

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Summary. Solvatochromic dinuclear mixed Ni(II)-complexes with one 1,2-diacetyl-1,2-dibenzoyl-ethanate ($dadb^{2-}$) and two tetramethylethylenediamine (*tmen*) ligands have been prepared and characterized. The tetraphenylborate is orange with molecules in bis-square-planar configuration and the nitrate is green with molecules in a bis-octahedral form. They have been investigated by UV, Vis, IR, and Far-IR spectroscopy as well as by electrochemical and magnetochemical methods. In strong donor solvents the nitrate ligands are replaced by solvent molecules. In weak donor solvents the anion-dependent equilibrium between the bis-planar, the bis-octahedral and an intermediate planar-octahedral form was investigated.

Keywords. Nickel(II)complexes, solvatochromism; Tetramethylethylenediamine; Tetraketones.

Spektroskopische und elektrochemische Untersuchungen an zweikernigen gemischten Ni(II)-Chelaten

Zusammenfassung. Solvatochrome zweikernige Ni(II)-Komplexe mit einem 1,2-Diacetyl-1,2-dibenzoylethanat ($dadb^{2-}$) und zwei Tetramethylethylenediamin (*tmen*)-Liganden wurden hergestellt und charakterisiert. Das Tetraphenylborat ist orangefarbig und enthält Komplexe in bis-quadratisch-planarer Anordnung. Das Nitrat ist grün mit Molekülen in bis-oktaedrischer Form. Die Untersuchungen erfolgten mit Hilfe der Spektroskopie im UV-, im sichtbaren, im IR- und im Far-IR-Bereich sowie elektrochemischer und magnetischer Methoden. In starken Donor-Lösungsmitteln sind die Nitratliganden durch Solvens-Moleküle ersetzt. In schwachen Donor-Lösungsmitteln wurde das von den Anionen abhängige Gleichgewicht zwischen der bis-planaren, der bis-oktaedrischen sowie der intermediären planar-oktaedrischen Form untersucht.

Introduction

Mixed chelates of Ni(II) with a diamine and a β -diketonat appear either in a square planar configuration, or – in the presence of donor molecules – in octahedral geometry. They show solvatochromic and thermochromic behaviour [1–7]. The mononuclear complex, $[\text{Ni}(\textit{tmen})(\textit{acac})]^+$ (*tmen* = tetramethylethylenediamine; *acac* =

** Dedicated to Professor Dr. Edwin Hengge on occasion of his 60th birthday

acetylacetonate) can be used as a color indicator for the solvent donor strength [8–13]. Coordinating anions like NO_3^- and acad^- may compete for ligand sites at the Ni-coordination center with poorly coordinating solvent molecules such as 1,2-dichloroethane (*DCE*) or nitroethane (*NE*) [12–16].

We wish to report about new dinuclear Ni-complexes with a tetradentate ligand [17], namely 1,2-diacetyl-1,2-dibenzoylethanate (dadb^{2-}) by which two Ni-coordination-centers are linked. As in the case of the monomeric complexes solvatochromism and anion-dependent structural features due to the change between square planar and octahedral coordination at the coordination centers were observed. The investigation of spectroscopic, vibrational and electrochemical behaviour of the dinuclear complexes brought insight into structural changes within these complexes due to donor-molecules or anions.

Experimental

Starting materials for the synthesis of the ligand 1,2-diacetyl-1,2-dibenzoylethanate, as described in the following, were obtained from Dojindo Laboratories (extra pure) and have been used without further purification. Solvents used for spectral, conductivity and polarographic measurements have been purified according to standard procedures [18] or were of "spectral grade". Other solvents and ligands were purified as described elsewhere [19–21]. The water content in the solvents was measured by Karl-Fischer titration and usually found less than 30 mg/dm^{-3} .

1,2-Diacetyl-1,2-dibenzoylethane (H_2dadb)

The method used was based on that by Charles et al. [22] including some modifications: 18.4 g (0.1 mmol) of well-dried sodiumbenzoylacetate (*Nabzac*) ground to a fine powder were suspended into 450 ml of ether under vigorous stirring. Then 13.0 g (0.05 mmol) of I dissolved in 150 ml of ether were added drop-wise within about 2 hours. Using a rotating evaporator the solvent was almost completely removed from the solution. The obtained crude solid was suspended into 500 ml of H_2O under vigorous stirring. The remaining precipitate was filtered and recrystallized twice from methanol (*MeOH*) yielding about 35% of the stoichiometric amount. The results of the elementary analysis are given in Table 1.

$\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$

1.84 g (5 mmol) of Hdadb and 0.56 g (10 mmol) KOH suspended in 30 ml ethanol (*EtOH*) were added under continuous stirring to a solution containing 2.90 (10 mmol) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 ml *EtOH* yielding a pale bluish-green solution. To this 1.285 g (11 mmol) of tetramethylethylenediamine (*tmen*) were added drop-wise under stirring. After heating, the color of the solution turned green. KNO_3 was removed by filtration. Crude crystals obtained after 2 days were recrystallized from 1,2-dichloroethane (*DCE*) to give pale blue crystals in 58% yield.

$\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$

3.05 g (5 mmol) of the obtained $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$, were dissolved in 150 ml *DCE* and 3.76 g (11 mmol, i.e. twice excess) of NaBPh_4 were added as a finely ground powder under vigorous stirring, changing the solution from green to red. After the reaction was completed after about one hour of stirring, the solution was filtered to remove NaNO_3 and the remaining NaBPh_4 , and kept for 2 days at room temperature. The obtained red crystals were recrystallized from *DCE* with a yield of 80%.

Characterization of the Complexes

Electronic spectra of solutions were obtained with a Hitachi 340 recording spectrometer and a Cary 17 D spectral photometer using 10 mm quartz cells at constant temp. (25 °C). Powder reflectance spectra were recorded with the former instrument, attached with an integrating sphere, using BaSO₄ as a reference. Infrared spectra were recorded from nujol mulls using a Perkin Elmer 457 Grating Spectrometer (5 000–400 cm⁻¹). Far infrared spectra were measured with a Nicolet 20 F-FTIR spectrometer. Electric conductances of the solutions were measured with a Conductivity Outfit Model AOC-10 (Denki-Kagaku-Keiki Co. Ltd) at 25 ± 0.2 °C. Magnetic susceptibility measurements were performed by a Faraday method with a Shimadzu Torsion Magnetometer MB-100 at room temperature.

For polarographic measurements a standard polarographic setup from Texas Instruments was used as described elsewhere [23–25]. A nonisothermal cell arrangement was used with a silver wire reference electrode kept at constant temperature. Solutions containing 0.1 mmol dm⁻³ of the dinuclear Ni-complex and 0.1 mmol dm⁻³ of NBu₄Ph₄ were placed in a thermostated double-sided cell and pure nitrogen was passed through the solution during the experiment. Cyclic voltammetry was performed on platinum or on carbon-glass electrodes. For the polarographic measurement either bis-(biphenyl)-chromium(I)-tetraphenylborate (BBCr) [26] or ferrocene was used as reference. All potentials are given versus the former. The number of electrons transferred by each of the steps was obtained by plotting the cyclic voltammetric peak current versus the square root of the scan rate, yielding straight lines with characteristic slopes [27].

Results and Discussion

The reflectance spectra of the solid dinuclear complexes (Fig. 1) are similar to those of the monomeric chelates reported earlier [1–8, 11]. For the tetraphenylborate the strong band at 472 nm (21.2 · 10³ cm⁻¹) can be assigned [28] to a ¹A_{2g} ← ¹A_{1g} (i.e. d_{x²-y²} ← d_{xy}) transition in analogy to the monomeric square planar Ni(II) complexes. The dinuclear nitrate shows two absorption bands at 1 053 nm (9.5 · 10³ cm⁻¹) and at 617 nm (16.2 · 10³ cm⁻¹) which can be assigned to a ³T_{2g} ← ³A_{2g} transition (corresponding directly to Δ) and to a ³T_{1g}(F) ← ³A_{2g} tran-

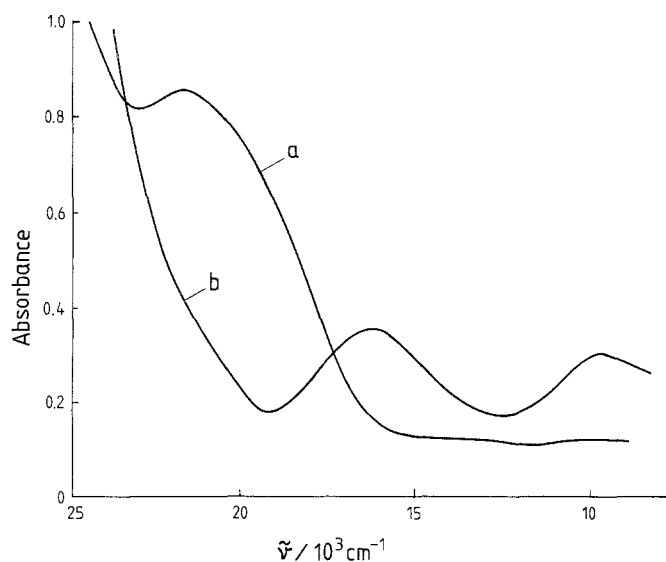


Fig. 1. Solid state reflectance spectra of Ni₂(*dadb*)(*tmen*)₂(BPh₄)₂ (a) and Ni₂(*dadb*)(*tmen*)₂(NO₃)₂ (b)

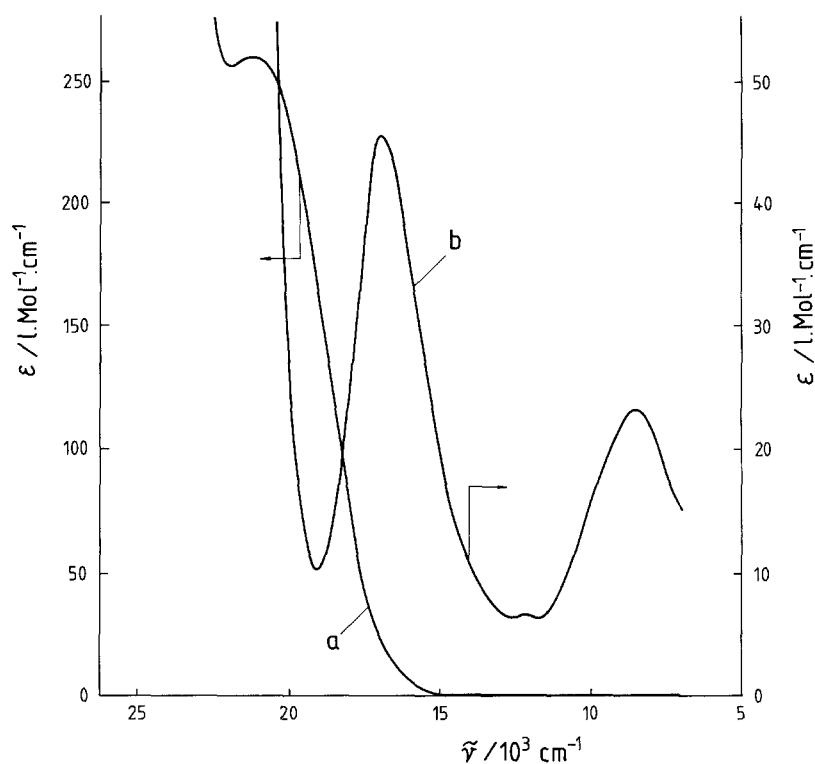


Fig. 2. Absorption spectra of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ (a) and of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ (b) in DCE solutions

Table 1. Analytical data, magnetic moments (μ), molecular weights (M.w.) and melting points (M.p.)

| Compound | %C | %H | %N | M.p./°C | μ/BM | M.w. |
|---|----------------------------|--------------|----------------|----------------------|-------------------|---------|
| H_2dadb | Found 74.32 Calc. 74.52 | 5.75 5.63 | — | 189–209 | | |
| $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ (orange) | Found 73.22 Calc. 73.43 | 6.73 6.78 | 4.30 4.28 | 224–225 | Dimagnetic | 1 308.6 |
| $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ (yellowish green) | Found 47.62 Calc. 48.40 | 6.00 6.09 | 10.78 10.58 | 237–242 ^a | 3.14 ^b | 766.2 |

^a Under decomposition

^b At 25°C, value given per one nickel ion

sition in analogy to the octahedral mononuclear complexes [1, 2, 7, 11]. The shoulder near 450 nm may be associated with the ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$ transition.

In DCE-solutions the spectra of the complexes are similar to those in the solid state. The small absorption band observed at the nitrate at 660 nm may be assigned to a ${}^1\text{E}_g \leftarrow {}^3\text{A}_{2g}$ transition (see Fig. 2). The spectra obey Beer's law and hence no significant dissociation of the NO_3^- ligand appears to take place.

Table 2. IR-absorption frequencies of dinuclear and the comparable mononuclear complexes and their assignments

| Ni ₂ (<i>dadb</i>)(<i>tmen</i>) ₂ (BPh ₄) ₂ | Ni(<i>bzac</i>)(<i>tmen</i>)BPh ₄ | Ni ₂ (<i>dadb</i>)(<i>tmen</i>) ₂ (NO ₃) ₂ | Ni(<i>bzac</i>)(<i>tmen</i>) NO ₃ | Assignment |
|--|--|---|--|---------------------------------|
| – | – | 1 765 | 1 767 | v NO ₃ [–] |
| – | – | 1 720 | 1 717 | v NO ₃ [–] |
| 1 590 | 1 585 | 1 590 | 1 597 | v C=O |
| 1 550 | 1 555 | 1 570 | 1 575 | v C=C |
| 1 485 | 1 520 | 1 500 | 1 520 | v C=C |
| – | – | 1 290 | 1 285 | v NO ₃ [–] |
| 625 | 625 | – | – | v BPh ₄ [–] |

The tetraphenylborate Ni₂(*dadb*)(*tmen*)₂(BPh₄)₂ is diamagnetic, the Ni(II)-ions are of low-spin, and in the bis-square-planar form (Table 1). The two square planar subunits are orthogonally twisted to each other [17]. The nitrate Ni₂(*dadb*)(*tmen*)₂(NO₃)₂, is paramagnetic and in the bis-octahedral form. Conductivity measurements in weak donor solvent like *DCE* have shown that IO₃[–]-ions and BPh₄[–]-ions do not coordinate significantly to the Ni(II) center, whereas the NO₃[–]-ions are strongly coordinated [15, 17]. X-ray diffraction has shown that NO₃[–]-ions yield octahedral coordination [1, 2, 15], and that the nitrate ion acts as a bidentate and occupies two *cis*-positions. The IR absorption frequencies are given in Table 2 and the absorption maxima observed in the Far-IR region between 650 cm^{–1} and 50 cm^{–1} are given in Table 3. The observed bands are assigned according to the assignments based on normal coordinate analyses of similar complexes, namely of Ni(*acac*)₂ [29] and of Ni(*acad*)₂Py₂ [30–32] and on the spectra of NaNO₃ and NaBPh₄ to identify absorptions due to the anion. The absorption bands are similar for the dinuclear and the mononuclear Ni-complexes and hence the mutual interactions between the two Ni-coordination centers seem to be small (this is supported by the also almost unchanged UV-Vis-spectra).

The characteristic IR-absorption frequency of the nitrate ion (a weak combination band ν_1 and ν_4) in the dinuclear, bis-octahedral complexes is split into two bands at 1765 cm^{–1} and at 1720 cm^{–1} showing that the nitrate ion acts as a bidentate ligand [15, 16, 32]. Absorptions associated with Ni–O stretching vibrations are significantly shifted towards lower energies when BPh₄[–] is replaced by NO₃[–]. This is found for Ni–O stretching vibrations and for more complicated vibrations including ring deformation of the coordinated ketone. When the NO₃[–] is coordinated the Ni–O-bond strengths are decreased in agreement with the first bond length variation rule [10]. Accordingly, the square planar complex is low-spin with stronger metal-ligand bonds than the octahedral complex which is high spin. While the C=O bond seems to be strengthened when NO₃[–] is coordinated to Ni(*bzaz*)(*tmen*)⁺, in agreement with the second bond length variation rule [10], the respective band remains unchanged in the dinuclear complexes. The C=C bonds are found to be strengthened in these complexes when NO₃[–] is coordinated, whereas it is weakened in case of Ni(*acac*)(*tmen*)⁺ [2, 15, 16]. Although similar effects are also expected for the Ni–N-bonds to the *tmen* ligands the assigned Ni–N-vibrations are found to be almost invariant towards the anion.

Table 3. Far IR-data (ν/cm^{-1}) of the dimeric complexes (s=strong, m=medium, w=weak absorption band)

| $\text{Ni}_2(\text{dabd})(\text{tmen})_2(\text{BPh}_4)_2$ | | $\text{Ni}(\text{bzac})(\text{tmen})\text{BPh}_4$ | | $\text{Ni}_2(\text{dabd})(\text{tmen})_2(\text{NO}_3)_2$ | | $\text{Ni}(\text{bzac})(\text{tmen})\text{NO}_3$ | | Assignment |
|---|----------|---|----------|--|----------|--|----------|---------------------|
| Solid state | In DCE | Solid state | In DCE | Solid state | In DCE | Solid state | In DCE | |
| – | 639.02 m | – | 645.52 m | – | – | – | – | |
| 623.94 m | 624.05 m | 624.78 m | 624.17 m | 621.67 m | – | 617.50 m | – | |
| 610.35 s | 613.30 s | 612.30 s | 612.40 s | – | – | – | – | Ni–BPh ₄ |
| – | – | – | – | 600.02 m | 600.03 w | 604.81 m | – | Ni–NO ₃ |
| – | – | – | – | 590.70 m | 594.00 w | – | – | |
| 595.71 w | – | 590.54 w | 594.06 m | 585.81 m | 588.20 m | 589.29 s | 589.71 s | Ni–O ^a |
| 587.25 m | 588.21 m | 576.84 s | 578.56 m | 567.37 m | 568.89 m | – | – | Ni–O ^a |
| – | – | – | – | 553.56 s | 557.9 m | 531.56 s | 531.97 m | Ni–NO ₃ |
| 528.63 m | 533.17 m | 530.61 m | 530.25 m | – | – | – | – | Ni–BPh ₄ |
| 505.00 w | 505.00 w | 509.36 m | 512.97 m | 492.84 m | 493.65 m | 494.30 s | 493.64 m | Ni–O ^b |
| – | – | – | 501.47 m | 481.03 s | 486.23 w | – | – | Ni–O ^b |
| 490.87 w | 480.00 w | 492.58 m | 493.44 m | 450.79 m | – | – | 446.55 m | |
| 467.60 m | 468.92 m | 478.53 s | 478.26 m | 463.87 s | 469.73 m | 471.20 m | 467.77 m | Ni–O ^a |
| – | – | 467.90 s | 470.73 m | – | – | – | – | Ni–BPh ₄ |
| 441.57 w | 441.00 w | 441.57 s | – | 442.15 m | 447.88 m | 433.93 s | 428.25 m | Ni–O ^a |
| 418.93 m | – | 416.57 w | – | – | – | – | – | Ni–O ^b |
| 400.06 m | – | 405.32 m | – | 397.39 m | – | 409.05 w | 397.32 w | Ni–O ^b |
| – | – | 393.31 w | 375.72 m | 378.06 m | 382.33 s | 374.09 w | 375.90 w | Ni–O ^a |
| 343.35 w | 343.3 w | 341.38 m | 334.69 w | 334.05 m | – | 339.07 m | 340.41 m | Ni–O ^a |
| 310.00 w | 310.00 w | 315.00 w | 323.91 w | 313.65 m | 323.80 m | – | – | |
| 297.4 w | 298.2 w | 306.98 m | 302.23 w | – | – | – | – | Ni–BPh ₄ |
| 294.21 m | 281.37 m | 281.27 s | 280.68 s | 277.51 s | – | – | – | Ni–O ^b |
| 278.9 w | 291.00 w | – | – | – | – | – | – | Ni–BPh ₄ |
| 259.2 m | 261.26 m | 259.40 s | 268.01 s | 257.23 s | 262.30 s | 263.51 s | 260.62 m | Ni–O ^c |
| 227.43 w | 229.31 w | 231.60 s | 235.03 s | – | – | – | 221.19 m | Ni–O ^c |
| 201.37 w | 203.78 w | 202.57 s | – | 199.93 m | – | 202.59 s | 202.14 m | Ni–O ^c |
| 178.82 m | – | 182.16 m | – | 180.10 m | – | 177.09 m | 177.58 m | Ni–N |
| – | – | – | – | 167.19 m | – | – | – | |
| – | – | – | – | 151.37 w | – | 140.13 m | – | |
| – | 128.82 m | 127.03 w | – | 125.79 w | – | 129.00 w | 127.53 m | Ni–N |
| – | 119.35 w | 112.09 w | – | – | – | – | – | |
| – | – | 106.19 w | – | – | – | – | – | |
| – | – | 90.59 m | – | 94.52 w | – | 94.20 m | – | |
| – | – | – | – | 88.33 w | – | – | – | |
| 74.5 w | – | 80.87 s | – | 73.76 w | – | 69.66 w | – | |

^a Stretching vibration^b Asymmetric deformation of dabdb-plane^c Symmetric deformation of dabdb-plane

Polarographic and cyclic voltammetric techniques were used to investigate changes of enthalpic and entropic contributions to the free energies of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ and of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ in different solvents. Figs. 3 and 4 show the cyclic voltammograms measured on a carbon glass electrode for the two complexes dissolved in acetone. Two main oxidation waves together

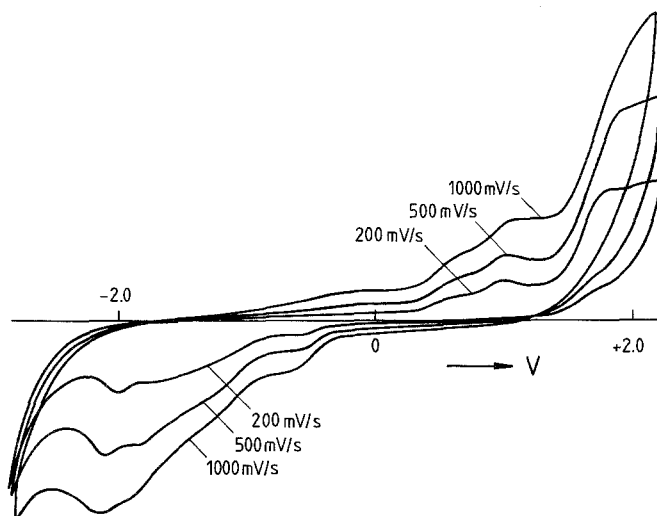


Fig. 3. Cyclic voltammogram for a solution $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ of $(10 \text{ mmol dm}^{-3})$ and NBu_4BPh_4 $(0.1 \text{ mol dm}^{-3})$ in *DCE*

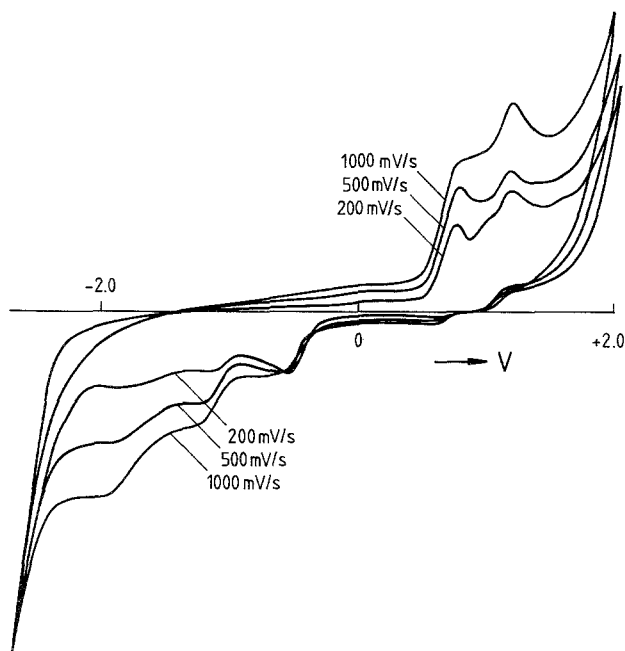
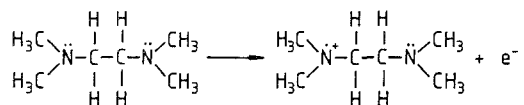


Fig. 4. Cyclic voltammogram for a solution of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ $(10 \text{ mmol dm}^{-3})$ and NBu_4Ph_4 $(0.1 \text{ mmol dm}^{-3})$ in *DCE*

with four reduction processes are observed, all of them being irreversible on both the carbon glass and the platinum electrode.

The oxidation processes can be regarded as the stepwise oxidation of *tmen* as given in the Schemes 1 and 2.

The observed reduction processes can be described by reaction schemes (Schemes 3–6), namely the reduction of the two Ni-coordination centers and the stepwise reduction of the bridging ketone.



Scheme 1

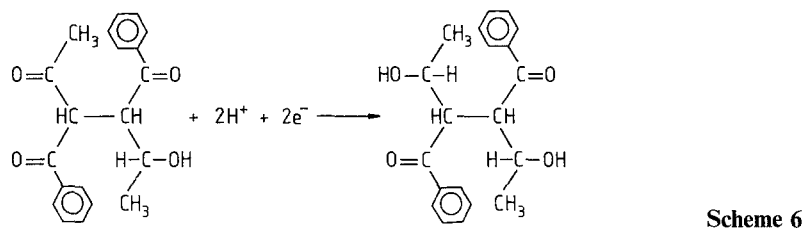
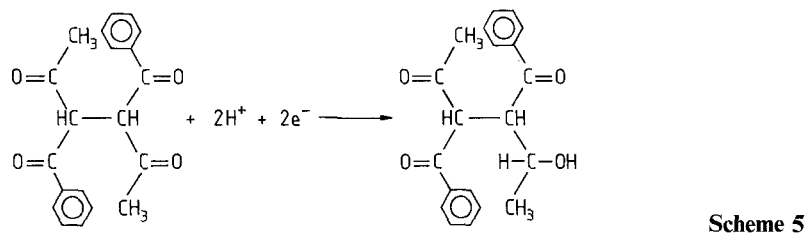
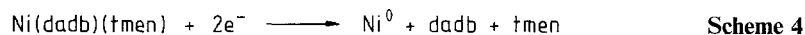
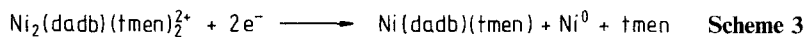
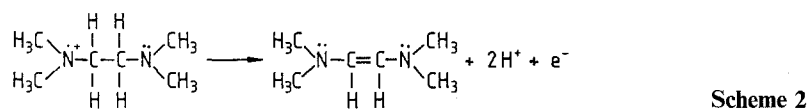


Table 4. Half wave potentials $E_{1/2}$ at 25 °C of the first Ni(II) reduction step, their temperature dependent part $dE_{1/2}/dT$ and their temperature independent part $E_{1/2}(T=0\text{ K})$

| Solvent | $E_{1/2}(T=298\text{ K})/\text{mV}$ | $dE_{1/2}/dT/\text{mVK}^{-1}$ | $E_{1/2}(T=0\text{ K})/\text{mV}$ | m^a | r^b |
|---|-------------------------------------|-------------------------------|-----------------------------------|-------|-------|
| $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ | | | | | |
| <i>DCE</i> | -532.1 | -1.66 | -38.78 | 5 | 0.976 |
| <i>An</i> | -528.1 | 2.86 | -1316 | 5 | 0.999 |
| <i>AC</i> | -589.4 | -1.21 | -227.7 | 5 | 0.999 |
| <i>EtOH</i> | -573.0 | 1.87 | -1130 | 5 | 0.995 |
| <i>DMF</i> | -735.8 | 1.36 | -1142 | 4 | 0.996 |
| <i>DMSO</i> | -690.8 | 2.09 | -1316 | 4 | 0.993 |
| $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ | | | | | |
| <i>DCE</i> | -595.9 | -1.36 | -191.3 | 6 | 0.980 |
| <i>AN</i> | -538.0 | 2.21 | -1196 | 5 | 0.996 |
| <i>AC</i> | -654.1 | -0.138 | -612.9 | 3 | 0.998 |
| <i>EtOH</i> | -552.4 | 3.40 | -1566 | 5 | 0.968 |
| <i>DMF</i> | -698.4 | -0.637 | -508.6 | 5 | 0.993 |
| <i>DMSO</i> | -682.8 | 1.77 | -1212 | 4 | 0.999 |

^a Number of data sets measured at different temperatures

^b Correlation coefficients for linear regression of $E_{1/2}(T)$ versus T

With common polarography at the dropping mercury electrode only the first Ni-reduction step could be resolved for all the investigated solvents (Table 4). analysis of the polarographic waves by differential pulse polarograms show that a further reduction process appears, exhibiting a much lower limiting current (in *EtOH* for $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ three separable Ni-reduction waves appear). With the exception of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ in *DMSO* the corresponding half-wave potentials are found at less negative potentials.

The two waves, exhibiting a separation of the two half wave potentials of up to 200 mV, cannot be due to separately observed redox properties of the two Ni-coordination centers, because they are also observed for the monomeric species. They cannot be due to differences in redox properties of the square-planar and of the octahedrally coordinated form because in **DCE** the two signals are found in the presence of either of them (i.e. dissolving either the BPh_4^- or the NO_3^- species). A titration procedure adding of *DMF* or *DMSO* to solutions of the square planar complexes in *DEC* confirmed this.

From investigations in aqueous systems it is known that Ni^{2+} sometimes exhibits catalytic pre-waves [33, 34]. When the Ni-complex is titrated in *DCE* with *tmen* a pre-wave is observed, which may be a catalytic one, due to free *tmen*-molecules in the electrode surrounding formed by reduction Ni^0 . Increasing temperature leads to a decrease of its limiting current until the signal completely vanishes above about 45 °C in all investigated solvents. This supports its interpretation as a catalytic a pre-wave.

The reduction potentials of the bis-square-planar BPh_4^- -complexes at 25 °C are nearly linearly related to the donor number. The $E_{1/2}$ values are more negative than those found for the comparable monomeric *bzac* complexes [the redox potentials of $\text{Ni}(\text{bzac})(\text{tmen})\text{BPh}_4$ are found [37] in *DCE* = -471 mV, in *DMF* = -647 mV, in *DMSO* = -727 mV] and this shows that the Ni(II-coordination centers are more stable towards reduction in the dinuclear species. The same conclusion is reached by comparing the bis-square-planar with the bis-octahedral complexes: As the coordination number is increased by solvent molecules or by coordinating NO_3^- -ions more negative Ni-reduction potentials are found, pointing to a decreasing free energy, i.e. an increasing stability of the coordination compound. The differences of the $E_{1/2}$ values between the NO_3^- and the BPh_4^- compounds are linearly related to the solvent donor number. In the strong donor solvent *DMSO* the $E_{1/2}$ values as well as the UV-Vis-spectra are nearly the same both for the (octahedral) nitrate and the (planar) tetraphenylborate. This may be due to substitution of the nitrate ligands by *DMSO* molecules. The difference of the $E_{1/2}$ values and of UV-Vis spectra decrease in the solvent series $\text{DMSO} \geq \text{An} > \text{DMF} > \text{Ac} \geq \text{DCE}$. *Ac* is coordinated scarcely probably due to a sterically hindered coordination towards the Ni-center. This is in agreement with results found at the mononuclear species. The $E_{1/2}$ values obtained in *DMSO* and *An* solutions are approximately the same for the NO_3^- and the BPh_4^- species, whereas the values differ significantly for the solvents *DCE*, *Ac*, *An*, *EtOH*, and *DMF*. This suggests that the NO_3^- is completely removed and exchanged by *DMSO* molecules and unexpectedly also by *An* molecules. (This explains the surprising position of *An* within the above given sequence of the differences of $E_{1/2}$ values.) The differences in the UV-Vis spectra between BPh_4^- and NO_3^- complexes are largest in *DCE* and *Ac* and decrease with increasing donor number of the solvent. The temperature dependence of the $E_{1/2}$ values,

however, remain different for the two anion species even for strong coordinating solvents. The half wave potential of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ in *DCE* is found to be lower as expected from the linear relationship with the donor numbers which can be interpreted either by the donor properties of *DCE* [39] or by ion-pair formation [12, 14]. The inertness of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ is seen from the absence of correlations with the donor number or with the acceptor number. This may be due to competition between the coordination of one or two charged anions acting each as bidentates and coordination by solvent molecules.

A plot of the $E_{1/2}$ values observed in different solvents versus T yields straight lines with entropy related slopes and intercepts corresponding to the enthalpy of the reduction processes [24, 35, 36] (Figs. 5 and 6). The entropy related temperature coefficients of $E_{1/2}$ of the bis-square-planar complexes are linearly related to the donor number. The $dE_{1/2}/dT$ values decrease with increasing donor number and show negative values in *DMSO*. The enthalpy related $E_{1/2}(T=0\text{ K})$ values become less negative with increasing donor number, which might be an indication for a compensation effect [37–38]. A proper statistical analysis, however, did not yield a common isosolvent relationship [37, 39]. A necessary condition for the occurrence of an isoparameter relationship (i.e. an isokinetic, isoequilibrium, isosolvent relationship, etc.) is that the changes within the considered series can be associated with only one parameter (i.e. a general LFER condition) [40]. Figs. 5 and 6 show that this condition is not fulfilled. $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_2)_4_2$ yields two groups associated with different LFER conditions in *Anm*, *EtOH*, *DMSO*, and *DMF* and in *DCE* and *Ac*. In the former group of solvents the temperature coefficients of $E_{1/2}$ are positive and in the latter negative. The entropy changes are decreasing with more negative reduction potentials of the dissolved complex, i.e. with increasing donor number. The reduction of one Ni-coordination center leads to an entropy increase for the former group and to decreasing entropy in case of the latter. This increase in entropy may be connected with the reduction to Ni^0 and hence the destruction of the complex. This is in agreement with the entropy differences between the bis-square-planar (BPh_4^- in *DCE* and *Ac*) and the bis-octahedral (NO_3^- and BPh_4^- in *An*, *EtOH*, *DMSO*, and *DMF*) complexes. In *DCE* (due to its low donor number) and in *Ac* (due to sterical hindrance) square planar complexes are present and the entropy increase due to the destruction of the complex is overcompensated by the entropy decrease due to the electron transfer process itself.

The temperature dependence of the reduction potentials of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ in different solvents is obviously complicated because of the appearance of a solvent-anion exchange reaction. With the exception of *DMF* the same sequence of the solvents is found although no isoentropic behaviour is occurred. The $E_{1/2}$ values for *Ac* shows almost no temperature dependence, i.e. no entropy changes occur. The values in *DCE* and in *DMSO* (complete replacement of the nitrate by two *DMSO* molecules) remain almost unchanged whereas the values for *DMF* exhibit an entropy decrease with the reduction process.

It might be pointed out that the reduction potentials shift towards more negative values when going from the monomeric ($E_{1/2} = -471\text{ mV}$ for $\text{Ni}(\text{bzac})(\text{tmen})\text{BPh}_4^-$ in *DCE*), to the bis-square-planar ($E_{1/2} = -532.1\text{ mV}$ for $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ in *DCE*), to the bis-square-planar ($E_{1/2} = -532.1\text{ mV}$ for $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ in *DCE*) and further to the bis-octahedral species ($E_{1/2} = -595.9\text{ mV}$ for $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ in *DCE*) with about equal differences.

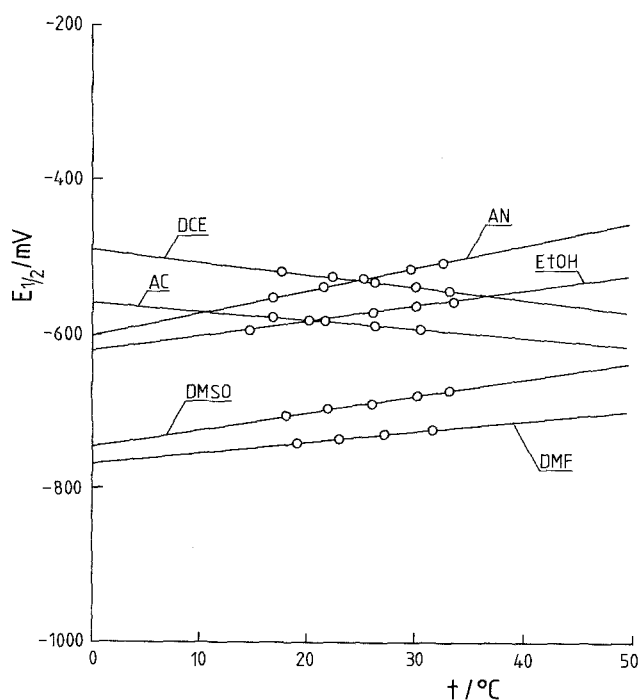


Fig. 5. Polarographic half wave potentials ($E_{1/2}$) of the first Ni-reduction process versus temperature for $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ in different solvents

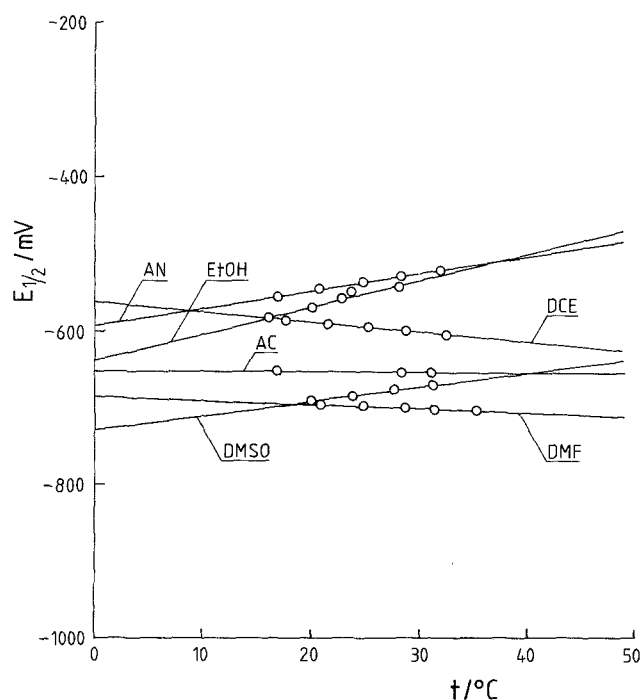
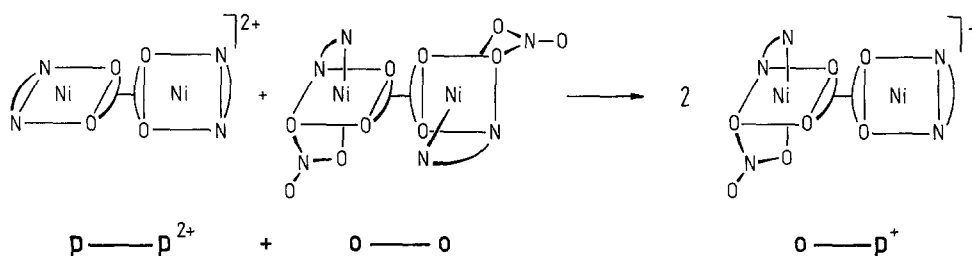


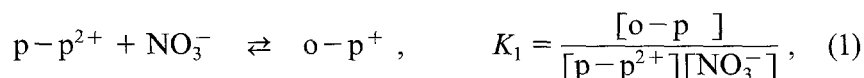
Fig. 6. Polarographic half wave potentials ($E_{1/2}$) of the first Ni-reduction process versus temperature for $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ in different solvents

According to this the Ni-coordination center is more stabilized in the dimeric complex than in the monomeric complex in agreement with the stronger acidity of *dadb* ($pK_1 = 9.90$, $pK_2 = 12.37$ as resulting from *pH*-metric titration) in comparison to *bzac* ($pK = 13.23$).



Scheme 7

By addition of NO_3^- ions to a solution of the bis-square-planar BPh_4^- complex ($p-p^{2+}$) a stepwise coordination of nitrate ions via an octahedral-planar form ($o-p^+$) as an intermediate to the bis-octahedral form ($o-o$) may be assumed. The equilibrium constants K_1 and K_2 of the processes



and



cannot be obtained by spectroscopic titrations because the spectrum of a solution of $o-p^+$ is hardly distinguishable from that of the mixture of $o-o$ and $p-p^{2+}$ [42].

In order to find access to K_1 and K_2 we have investigated the related equilibrium shown in Scheme 7 with the corresponding equilibrium constant K by means of solutions containing constant overall Ni concentrations with varying initial concentrations of the BPh_4^- complex (i.e. $p-p^{2+}$) and of the NO_3^- complex (i.e. $o-o$),

$$K = \frac{[o-p^+]^2}{[o-o][p-p^{2+}]}. \quad (3)$$

The concentration setup was chosen to obey linearly decreasing initial concentration of $p-p^{2+}$ paralleled by linearly increasing initial $o-o$ concentration. Under these circumstances, for $K=0$ at least one isosbestic point is expected to appear *over the whole concentration range* at an absorption frequency, namely at a wave length where the molar absorptions of the $p-p^{2+}$ and of the $o-o$ spectra are equal. In case of large K (i.e. $K=\infty$) two different ranges are expected, one for excess in $[o-o]_0$ and another one for excess in $[p-p^{2+}]_0$ concentration.

In each range only two species are present, namely in the former $o-o$ and $o-p^+$ and in the latter $p-p^{2+}$ and $o-p^+$. This means that in the case of large K at least two isosbestic points are expected, i.e. one in the presence of excess of $[p-p^{2+}]_0$, and one in the presence of excess of $[o-o]_0$. When passing from one to the other concentration region the respective isosbestic points are expected to disappear. They are expected at wave numbers where either $o-o$ and $o-p^+$ or $p-p^{2+}$ and $o-p^+$ have equal molar absorptions. To visualize this situation the concentrations of $p-p^{2+}$, $o-o$, and $o-p^+$ and the resulting spectral absorption were calculated using the formulas given below for several K values (including the extreme cases of $K=0$ and $K=\infty$) and are plotted for an isosbestic wavelength (Fig. 7).

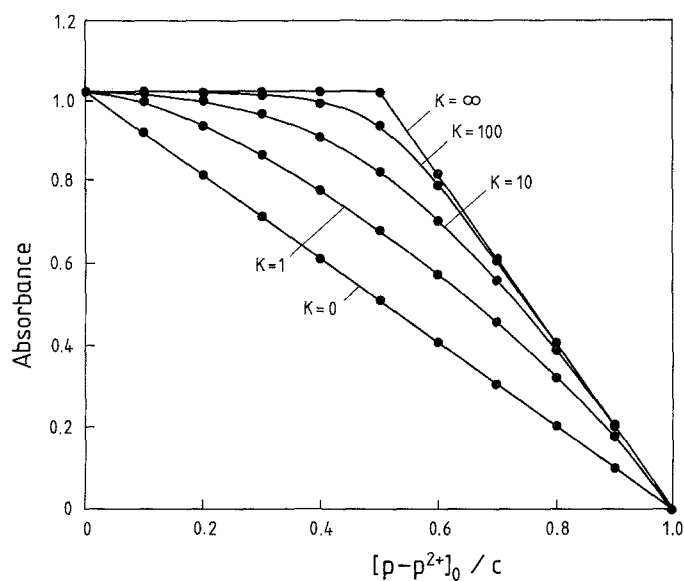


Fig. 7. Spectral absorbance calculated for different K -values at the isosbestic point at $21.7 \cdot 10^3 \text{ cm}^{-1}$ (i.e. 461 nm) versus the initial concentration of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ divided by the overall concentration

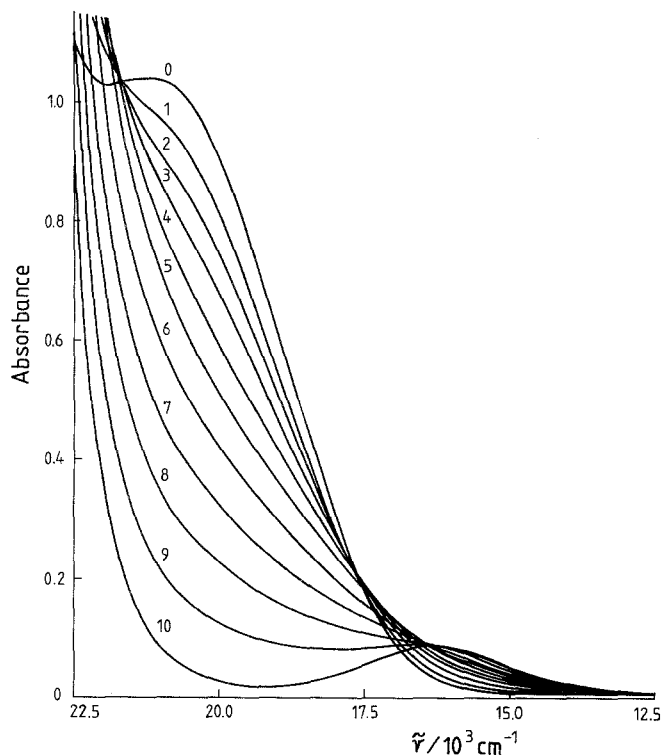


Fig. 8. Absorption spectra of $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{BPh}_4)_2$ and $\text{Ni}_2(\text{dadb})(\text{tmen})_2(\text{NO}_3)_2$ in *DCE* with an overall Ni concentration of $0.004 \text{ mol dm}^{-3}$ at 25°C . Initially weighed concentrations are: 0: $[\text{p}-\text{p}^{2+}]_0/c=0$; 1: $[\text{p}-\text{p}^{2+}]_0/c=0.1$; 2: $[\text{p}-\text{p}^{2+}]_0/c=0.2$; etc., respectively, 0: $[\text{o}-\text{o}]_0/c=1.0$; 1: $[\text{o}-\text{o}]_0/c=0.9$; 2: $[\text{o}-\text{o}]_0/c=0.8$; etc.

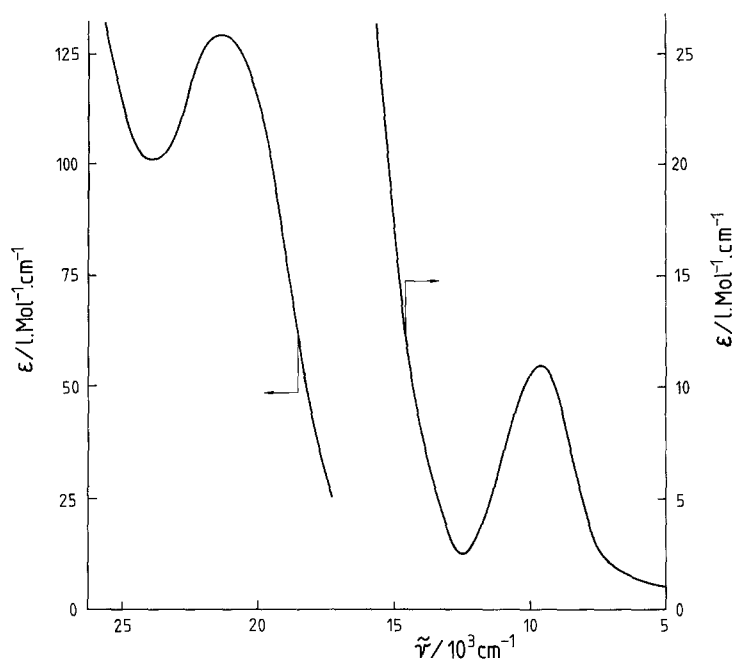


Fig. 9. Calculated absorption spectrum of the species $o-p^+$ i.e. $Ni_2(dadb)(tmen)_2(BPh_4)(NO_3)$ as resulting from the fitting procedure described in the text

The experimental spectra (Fig. 8), obtained under the above conditions for the initial concentrations show that the actual K value appears to be within the region accessible with this method. The expected isobestic points are found at 461.9 nm and 574.7 nm in the range of a concentration ratio of $[p-p^+]/[o-o]_0$ between 0 and up to about 0.5 as well as at 611.6 nm when the concentration ratio was above 0.5.

With Eqs. (4)–(6)

$$x = 2[o-p^+] , \quad (4)$$

$$[o-o] = [o-o]_0 - x , \quad (5)$$

$$[p-p^{2+}] = [p-p^{2+}]_0 - x , \quad (6)$$

Eq. (3) can be rewritten as

$$K = \frac{4x^2}{([o-o]_0 - x)([p-p^{2+}]_0 - x)} . \quad (7)$$

Using the stoichiometry of reaction Scheme 7 one gets

$$x = \frac{[o-o]_0 K + [p-p^{2+}]_0 K + \sqrt{\{[o-o]_0 K + [p-p^{2+}]_0 K\}^2 - 4(K-4)[o-o]_0 [p-p^{2+}]_0 K}}{2(K-4)} . \quad (8)$$

The measured spectral absorption E in dependence of the initial concentrations is given by

$$E = 2x \varepsilon_{op} + \varepsilon_{oo}([o-o]_0 - x) + \varepsilon_{pp}([p-p^{2+}]_0 - x) . \quad (9)$$

In Eq. (9) E is expressed in terms of the weighed $[o-o]_o$ and $[p-p^{2+}]_o$ concentrations depending on two unknown parameters, namely K and ε_{op} (i.e. the extinction coefficient of $o-p$). Including the condition $[o-p^+] \leq [o-o] + [p-p^{2+}]$ K and ε_{o-p} have been evaluated using a Marquart least square fitting procedure [41] for overall complex-concentrations of 0.002 and 0.005 M , respectively. Because of the functional dependence upon the wavelength the best values for K are expected near the isosbestic points, yielding $K=96 \pm 3$. This value was used for fitting a spectrum of the $[o-p^+]$ species, which is given in Fig. 9, where the absorption band at the right hand side refers to the octahedrally coordinated Ni center and the band at the left hand side to the planar coordinated part of the molecule.

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