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Reactivity of five- and six-coordinated solvates. A complex formation and crystallographic study of the nickel(II) bromide and iodide systems in dimethyl sulfoxide and *N*,*N′*-dimethylpropyleneurea †

Dorota Bobicz,‡ Olof Kristiansson and Ingmar Persson *

Department of Chemistry, Swedish University of Agricultural Sciences, P.O. Box 7015,
SE-750 07 Uppsala, Sweden. E-mail: Ingmar.Persson@kemi.slu.se

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The complex formation equilibria for the nickel(II)-bromide and -iodide systems in dimethyl sulfoxide and the bromide system in *N*,*N′*-dimethylpropyleneurea have been studied calorimetrically and spectrophotometrically at 298 K. An ionic strength of 0.1 mol dm^{-3} was kept constant using tetrabutylammonium perchlorate as supporting electrolyte. Two stable mononuclear bromo-complexes are formed in dilute *N*,*N′*-dimethylpropyleneurea solution with $\beta_1 = (2.0 \pm 0.4) \times 10^3$ mol^{-1} dm^3 and $\beta_2 = (7.2 \pm 1.5) \times 10^5$ mol^{-2} dm^6, whereas nickel(II) does not form any measurable complexes with bromide and iodide ions in dimethyl sulfoxide solution. The structures of the solids precipitating from concentrated solutions of nickel(II)-bromide and -chloride in the respective solvents have been determined by X-ray diffraction. The solid precipitating from a concentrated *N*,*N′*-dimethylpropyleneurea solution of nickel(II) bromide is a stable pseudotetrahedral bis(*N*,*N′*-dimethylpropyleneurea)dibromonickel(II) complex. Precipitation of nickel(II) chloride from a dimethyl sulfoxide solution results in hexakis(dimethyl sulfoxide)nickel(II) tetrachloronickelate(II), which is gradually transformed to hexakis(dimethyl sulfoxide)nickel(II) chloride, the most enthalpy stabilised complex. Hexakis(dimethyl sulfoxide)nickel(II) bromide precipitates from a concentrated dimethyl sulfoxide solution of nickel(II) bromide.

Introduction

Complex formation reactions in solution are always in competition with solvation of the species involved, and are consequently strongly influenced by the solvating properties of the solvent. Therefore in general the stability of complexes increases with decreasing solvating ability of the solvent. This study will focus on another factor scarcely discussed before, the influence of steric restrictions of the metal ion solvate, exemplified by complex formation in the nickel(II)-bromide system in dilute dimethyl sulfoxide and *N*,*N′*-dimethylpropyleneurea solution.

Nickel(II) forms weak complexes with fluoride ions in aqueous solution (log $K_1 = 1.32$),[1] while nickel(II) complexes with the other halide ions are extremely weak (log $K_1 < -0.8$).[2,3] The degree of complex formation in a concentrated aqueous solution of nickel(II) chloride seems to increase with increasing temperature.[4] The complex formation of the nickel(II) halide system is in general expected to be stronger in aprotic non-aqueous solvents than in water,[5] mainly due to the weaker solvation of halide ions in such solvents.[6] The nickel(II) ion is expected to be only slightly more strongly solvated in solvents such as dimethyl sulfoxide and *N*,*N*-dimethylformamide than in water, while acetonitrile generally solvates metal ions more weakly than water, except for monovalent d^{10} metal ions.[7] Significant complex formation between nickel(II) and chloride is reported in methanol (log $K_1 = 2.82$),[8] in dimethyl sulfoxide (log K_1 = 1.51–2.7, depending on ionic medium and strength)[9–11] and in *N*,*N*-dimethylformamide (log K_1 = 2.85–3.14).[12,13] *N*,*N*-Dimethylacetamide is the only solvent where complex formation between nickel(II) and bromide ions has been reported (log $K_1 = 2.57$).[14]

Structural studies of solvated metal ions in solution show that the coordination number of the transition metal ions is lower than six in some solvents where the solvent molecule is bulky. The nickel(II) ion is reported to be five-coordinated in 1,1,3,3-tetramethylurea[15] and four-coordinated in hexamethylphosphoric triamide.[16] The nickel(II) ion is five-coordinated, most probably in a square-pyramidal fashion, in *N*,*N′*-dimethylpropyleneurea, having a deep red colour.[17]

Complex formation reactions starting from a five-coordinated nickel(II) solvate have not yet been studied. In this study we report complex formation for the nickel(II) bromide system in dimethyl sulfoxide and *N*,*N′*-dimethylpropyleneurea, and of the nickel(II) iodide system in dimethyl sulfoxide; iodide systems cannot be studied in *N*,*N′*-dimethylpropyleneurea as the iodide ion is spontaneously oxidised to iodine.[18] The complex formation equilibria have been studied calorimetrically and spectrophotometrically at 298 K. The ionic strength of 0.1 mol dm^{-3} was kept constant using tetrabutylammonium perchlorate, $(C_4H_9)_4NClO_4$, as supporting electrolyte. We have also crystallographically characterised the solids precipitating from concentrated solutions of nickel(II)-chloride and -bromide in dimethyl sulfoxide and *N*,*N′*-dimethylpropyleneurea. By increasing the concentration, which is maximised in the solid state, only the enthalpically stabilised complexes will remain as stable species.[19]

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† Electronic supplementary information (ESI) available: Fig. S1: the fitting of the absorbance of the UV-vis spectra of nickel(II) bromide *N*,*N′*-dimethylpropyleneurea solutions. Figs. S2 and S3: the complex distribution function and the complex formation function, respectively. Fig. S4: the infrared and Raman spectra of the crystallographically studied solids. See http://www.rsc.org/suppdata/dt/b2/b204128f/

‡ Permanent address: Department of Physical Chemistry, Technical University in Gdansk, ul. Gabriela Narutowicza 11/12, PL-80-952 Gdansk, Poland.

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Experimental

Chemicals

Dimethyl sulfoxide (Merck, reagent grade) and *N*,*N′*-dimethylpropyleneurea (BASF) were distilled over calcium hydride (Fluka) under vacuum and stored in dark bottles over 3 Å molecular sieves. Tetrabutylammonium bromide, $(C_4H_9)_4NBr$, tetrabutylammonium iodide, $(C_4H_9)_4NI$, and perchlorate, $(C_4H_9)_4NClO_4$, (all Fluka, assay >99%) were used without further purification, but they were dried in a desiccator over phosphorus pentoxide under vacuum for several hours in an oven at 70 °C. Hexakis(dimethyl sulfoxide)nickel(II) perchlorate, $[Ni(OS(CH_3)_2)_6](ClO_4)_2$, **1**, was prepared as described elsewhere,[17] and recrystallized from dimethyl sulfoxide. Solid bis(*N*,*N′*-dimethylpropyleneurea)dibromonickel(II), $NiBr_2(OCN_2(CH_3)_2(CH_2)_3)_2$, **2**, was prepared by dissolving anhydrous nickel(II) bromide (Aldrich, 99.998+%) in *N*,*N′*-dimethylpropyleneurea until saturation at *ca.* 310 K, and deep blue **2** precipitated on slow cooling to room temperature. An *N*,*N′*-dimethylpropyleneurea solution of nickel(II) perchlorate was prepared by mixing nickel(II) bromide and silver(I) perchlorate solution in the molar ratio 1 : 2, and the silver bromide formed was centrifuged off. The volume of this solution was reduced by distillation, but it has not been possible to obtain any crystalline solvate. Hexakis(dimethyl sulfoxide)-nickel(II) chloride, $[Ni(OS(CH_3)_2)_6]Cl_2$, **3**, and hexakis(dimethyl sulfoxide)nickel(II) bromide, $[Ni(OS(CH_3)_2)_6]Br_2$, **4**, were prepared by dissolving anhydrous nickel(II)-chloride and -bromide, respectively, in freshly distilled dimethyl sulfoxide (Merck) until saturation at *ca.* 310 K. The initial crystals which precipitated from the chloride solution were blue hexakis(dimethyl sulfoxide)nickel(II) tetrachloronickelate(II), $[Ni(OS(CH_3)_2)_6][NiCl_4]$, **5**, which with time rearranged to green crystals of **3**. Vibrational spectra (infrared and Raman) have been recorded for identification, see Fig. S4.

Calorimetric measurements

Titration calorimetry, using a ThermoMetric 2277 TAM microcalorimeter, was used to determine the heat of complex formation between nickel(II), and bromide and iodide in dimethyl sulfoxide and *N*,*N′*-dimethylpropyleneurea solution at 298.15 ± 0.01 K. The titration vessel, 3.5 cm^3, was rhodium-plated for chemical inertness and the stirrer was a KEL-F cylinder on a gold axis. The start volume in the titrations was 3.0 cm^3 of a 3.0 mmol dm^{-3} solution of nickel(II) perchlorate in *N*,*N′*-dimethylpropyleneurea or a 2.0 mmol dm^{-3} solution of nickel(II) perchlorate in dimethyl sulfoxide solvent containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte. These solutions were titrated portionwise with 0.1 mol dm^{-3} solutions of tetrabutylammonium bromide in dimethyl sulfoxide and *N*,*N′*-dimethylpropyleneurea. In each titration point, 5.0 mm^3 of ligand solution was added by a computer-controlled pump driving a microliter syringe through a very thin gold capillary. In total 36 portions were added in each titration series. At least three titration series were performed for each system. In addition, the heats of dilution of the nickel(II) and bromide ions were performed by titration of a solution only containing supporting electrolyte. Two titration series for the dilution of nickel(II) and bromide ions in each solvent were performed. All heats of dilution were very small, which were used to correct the experimental heats of reaction. The stability constants and the corresponding enthalpy changes were calculated by means of the least-squares program KALORI.[20]

The calorimeter system was calibrated with the barium–18-crown-6 system in water. Obtained values for the used calorimeter: log K_1 = 3.74(2) and ΔH = 33.1(2) kJ mol^{-1}, literature data: log K_1 = 3.75 and ΔH = 33.1 kJ mol^{-1}.[21]

Spectrophotometric measurements

UV-Vis spectra of 13 *N*,*N′*-dimethylpropyleneurea solutions with a constant nickel(II) concentration, 0.02195 mol dm^{-3}, and varying concentration of bromide, 0.002–0.054 mol dm^{-3}, were measured in the range 350–800 nm with a Perkin-Elmer Lambda 2 double-beam spectrophotometer at 298 ± 1 K. The cell thickness used was 0.500 cm. Tetrabutylammonium perchlorate was used as supporting electrolyte to an ionic strength of 0.1 mol dm^{-3}. The stability constants and the molar absorption coefficients of the nickel(II) species were calculated by means of the least-squares program SPECTRUM.[22]

Single crystal X-ray diffraction

Data were collected on a Bruker SMART platform equipped with a CCD area detector and a graphite monochromator using Mo-Kα (λ = 0.71073 Å) radiation.[23] The temperature used was 295 ± 1 K. A hemisphere of data (1295 frames) was collected for each structure using the omega scan method (0.3° frame width). The crystal to detector distance was 5.0 cm. The first 50 frames were re-measured at the end of each data collection to monitor crystal and instrument stability. The intensity decay was negligible with the exception of hexakis(dimethyl sulfoxide)nickel(II) bromide dimethyl sulfoxide where a crystal decay of *ca.* 20% was observed. The data for this compound are therefore of limited quality but nevertheless included since firm conclusions can still be drawn. The ratio of observed to calculated reflections, the completeness to Θ_{max}, for hexakis(dimethyl sulfoxide)nickel(II) chloride, **3**, and bromide, **4**, is low (78.6 and 74.0%, respectively), which presumably is a result of a higher pseudo-symmetry causing systematic extinctions. In compound **5** one Ni–Cl bond of a $NiCl_4^{2-}$ ion lies on a four-fold axis giving a square pyramidal geometry. A completely unconstrained refinement of the occupancy factors gives 0.971 for the Cl atom in the apex position and 0.762 for the four symmetry related Cl atoms in the basal plane. With the constraint of having four Cl atoms we approximate this to the Cl atom in the apex position having occupancy 1 and the Cl atoms in the basal plane having occupancy 0.75. The structures were solved by direct methods in SHELXTL[24] and refined using full-matrix least squares on F^2. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were calculated in ideal positions riding on their respective carbon atom.

Crystal structure determination of complex 2. $C_{12}H_{24}Br_2N_4O_2Ni$, M = 474.87, monoclinic, a = 8.021(4), b = 8.554(5), c = 26.606(14) Å, β = 93.968(9)°, V = 1821.1(2) Å^3, T = 295 ± 2 K, space group $P2_1/c$ (no. 14), Z = 4, μ(Mo-Kα) = 5.462 mm^{-1}, 4040 reflections measured, 2270 unique (R_{int} = 0.0503) which were all used in the calculations. The final R_1 and $wR(F^2)$ ($I > 2\sigma(I)$) values are 0.0382 and 0.0866.

Crystal structure determination of complex 3. $C_{16}H_{48}Cl_2O_8S_8Ni$, M = 754.63, triclinic, a = 9.9520(16), b = 10.2209(16), c = 11.0282(18) Å, α = 64.208(4), β = 66.751(3), γ = 87.620(3)°, V = 916.4(3) Å^3, T = 295 ± 2 K, space group $P\bar{1}$ (no. 2), Z = 1, μ(Mo-Kα) = 1.163 mm^{-1}, 3140 reflections measured, 1895 unique (R_{int} = 0.0234) which were all used in the calculations. The final R_1 and $wR(F^2)$ ($I > 2\sigma(I)$) values are 0.0485 and 0.1157.

Crystal structure determination of complex 4. $C_{16}H_{48}Br_2O_8S_8Ni$, M = 843.55, triclinic, a = 9.900(5), b = 10.380(6), c = 11.295(6) Å, α = 63.608(12), β = 67.713(8), γ = 87.889(9)°, V = 949.8(9) Å^3, T = 295 ± 2 K, space group $P\bar{1}$ (No. 2), Z = 1, μ(Mo-Kα) = 3.084 mm^{-1}, 3076 reflections measured, 1346 unique (R_{int} = 0.0433) which were all used in the calculations. The final R_1 and $wR(F^2)$ ($I > 2\sigma(I)$) values are 0.1100 and 0.2355.

Table 1 Overall stability constants, β_n (mol^{-n} dm^{3n}), of nickel(II) bromide complexes in *N*,*N*′-dimethylpropyleneurea solution determined spectrophotometrically and calorimetrically at 25 °C, and the refined molar absorption coefficients, ε (mol^{-1} dm^{3}), at the four wavelengths, 724, 664, 635 and 449 nm, used in the calculations of the stability constants, ionic medium 0.1 mol dm^{-3} tetrabutylammonium perchlorate. NP = number of data points. The limits of errors refer to three standard deviations

Complex	β_n[a] Spectrophotometry	β_n[a] Calorimetry	ε_{724}	ε_{664}	ε_{635}	ε_{449}
$NiBr^+$	$(2.20 \pm 0.41) \times 10^3$	$(1.81 \pm 0.47) \times 10^3$	0	0	3 ± 1	12 ± 3
$NiBr_2$	$(6.5 \pm 1.4) \times 10^5$	$(9.2 \pm 4.2) \times 10^5$	56 ± 2	83 ± 2	78 ± 2	12 ± 3
Ni^{2+}			0	0	0	15 ± 3
NP	52	108	13	13	13	13

[a] Weighted mean overall stability constants: $\beta_1 = 2.02 \times 10^3$ mol^{-1} dm^3 and $\beta_2 = 7.2 \times 10^5$ mol^{-2} dm^6.

Crystal structure determination of complex 5. $C_{12}H_{36}Cl_4O_6S_6Ni_2$, M = 727.99, tetragonal, $a = b$ = 18.950(2), c = 8.5688(15) Å, V = 3077.0(8) Å^3, T = 295±2 K, space group $P4/n$ (no. 85), Z = 4, μ(Mo-Kα) = 2.002 mm^{-1}, 3511 reflections measured, 1695 unique (R_{int} = 0.0758) which were all used in the calculations. The final R_1 and $wR(F^2)$ ($I > 2\sigma(I)$) values are 0.0546 and 0.1348.

CCDC reference numbers 184727–184730.

See http://www.rsc.org/suppdata/dt/b2/b204128f/ for crystallographic data in CIF or other electronic format.

Vibration spectroscopy

The IR and Raman spectra of solutions and solid solvates were recorded at room temperature. The far-IR spectra were recorded in the range 50–500 cm^{-1} with a Perkin-Elmer 1700X spectrometer equipped with a deuterated triglycine sulfate, DTGS, detector and a KBr beam splitter. Polyethylene windows and 0.012 mm Teflon spacers were used for liquid samples and polyethylene pellets for the solids. For each far-IR spectrum 10000 scans were collected and averaged at a resolution of 4 cm^{-1}. A Perkin-Elmer 1720X spectrometer with DTGS detector and a Mylar beam splitter was used to record the mid-IR spectra in the range 400–4000 cm^{-1}. KBr windows were used for the liquid samples and a KBr matrix for the solids. In these measurements 100 scans were collected and averaged at a resolution of 4 cm^{-1}. The Raman spectra were obtained using a Renishaw system 1000 spectrometer, equipped with Leica DMLM microscope, diode laser (782 nm) and a Peltier cooled CCD detector.

Results

Spectrophotometric measurements

The stability constants of two mononuclear nickel(II) bromide complexes, and the molar absorption coefficients of these complexes and of the solvated nickel(II) ion in *N*,*N*′-dimethylpropyleneurea solution at 724, 664, 635 and 449 nm, were refined from the UV-vis spectra of 13 solutions with varying bromide : nickel(II) ratio (Figs. 1 and S1); the results are summarised in Table 1.

Calorimetric measurements

The titration calorimetric measurements showed the formation of two nickel(II) bromide complexes in *N*,*N*′-dimethylpropyleneurea, with the first step markedly endothermic and the second one slightly exothermic (Fig. 2). The calorimetric studies of the nickel(II)-bromide and -iodide systems in dimethyl sulfoxide showed that no complex formation takes place, and that the obtained heats at mixing nickel(II) and bromide/iodide were in total agreement with the heats of dilution. It was possible to calculate both stability constants and heats of complex formation from the calorimetric measurements in *N*,*N*′-dimethylpropyleneurea. In the final calculation of the heats of complex formation weighed mean values of the stability constants from the spectrophotometric and calorimetric measurements were held fixed. The thermodynamic functions obtained in the nickel(II) bromide system in *N*,*N*′-dimethylpropyleneurea are summarized in Tables 1 and 2; the complex distribution and formation functions are given in Figs. S2 and S3, respectively.

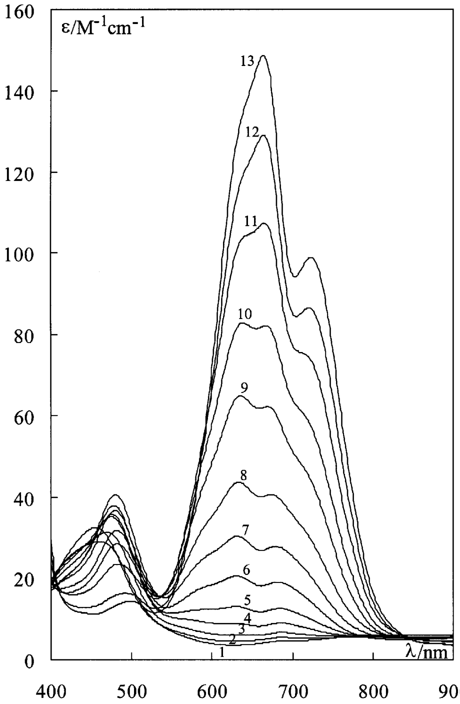

Fig. 1 UV-Vis spectra of nickel(II) bromide *N*,*N*′-dimethylpropyleneurea solutions with constant nickel(II) concentration, 21.95 mmol dm^{-3}, and varying bromide concentration: 1–2.0, 2–5.0, 3–7.0, 4–10.0, 5–13.0, 6–17.0, 7–21.0, 8–25.0, 9–32.0, 10–37.0, 11–44.0, 12–49.0 and 13–54.0 mmol dm^{-3}.

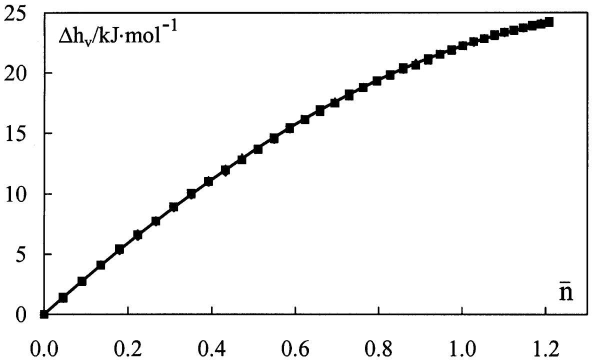

Fig. 2 The total molar enthalpy change, Δh_v, as a function of the ligand number n for the nickel(II) bromide system in *N*,*N*′-dimethylpropyleneurea. The symbols show different titration series and the solid line is calculated from the β_n and $\Delta H°_n$ values in Table 2.

Table 2 Overall enthalpy changes, $\Delta H^\circ_{\beta_n}$ (kJ mol^{-1}), determined calorimetrically, using the mean overall stability constants as fixed parameters, equilibrium constants, K_n (mol^{-1} dm^3), and thermodynamic functions, ΔG°_n, ΔH°_n (kJ mol^{-1}); ΔS°_n (J mol^{-1} K^{-1}), for the stepwise formation of nickel(II) bromide complexes in *N*,*N*′-dimethylpropyleneurea solution at 25 °C, ionic medium 0.1 mol dm^{-3} tetrabutylammonium perchlorate. The limits of error refer to three standard deviations

Complex	$NiBr^+$	$NiBr_2$
$\Delta H^\circ_{\beta_n}$	30.0 ± 0.4	23.9 ± 0.9
$\log K_n$	3.30 ± 0.07	2.56 ± 0.15
ΔG°_n	−18.8 ± 0.3	−14.6 ± 0.8
ΔH°_n	30.0 ± 0.5	−6.0 ± 1.5
ΔS°_n	164 ± 3	29 ± 8

Crystallography

The crystal structure of **2** is shown in Fig. 3a. The nickel(II) ion has an approximately tetrahedral geometry with the Br1–Ni–Br2 and O1–Ni–O2 angles being 126.11(3) and 105.83(12)°, respectively. The Ni–O distances are 1.946(3) and 1.951(3) Å whereas the Ni–Br distances are 2.3684(14) and 2.3724(11) Å. The Ni–O–C angles are 127.8(2) and 124.0(2)°, suggesting a "lone pair" coordination mode for the oxygen molecules. The *N*,*N*′-dimethylpropyleneurea ligands are, with the exception of the C3 and C13 atoms, approximately planar with an average deviation from the least-squares plane of 0.05 Å. In addition, the distances between the sp^3-hybridised carbon atoms in the propylene group, C2–C4 and C12–C14 are relatively short, with a mean value of 1.47(3) Å, suggesting a pseudo-aromatic character of the *N*,*N*′-dimethylpropyleneurea ligand. The dihedral angle between the two ligand planes is 85.5°.

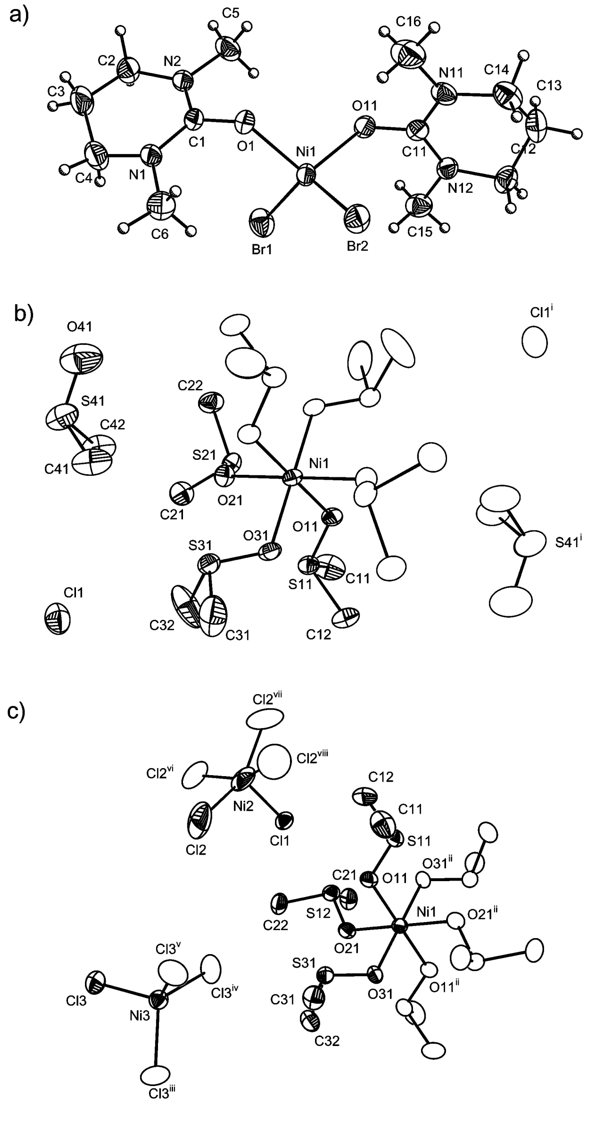

Fig. 3 Molecular structure of a) [Ni(*N*,*N*′-dimethylpropyleneurea)$_2$Br$_2$] (**2**), b) [Ni(OSMe$_2$)$_6$]Cl$_2$(Me$_2$SO)$_2$ (**3**) and c) [Ni(OSMe$_2$)$_6$][NiCl$_4$] (**5**). The displacement ellipsoids are shown at the 30% probability level for non-hydrogen atoms. Crystallographically independent atoms are shown with shaded ellipsoids whereas symmetry generated atoms are shown with empty ellipsoids. For clarity the hydrogen atoms are not shown in b) and c). [Symmetry codes: i) −*x*, −*y*, −*z*; ii) 1 − *x*, 1 − *y*, −*z*; iii) 1 − *y*, 1.5 + *x*, 1 − *z*; iv) −0.5 + *y*, 1 − *x*, 1 − *z*; v) 0.5 − *x*, 1.5 − *y*, *z*; vi) *y*, 1.5 − *x*, *z*; vii) 1.5 − *x*, 1.5 − *y*, *z*; viii) 1.5 − *y*, *x*, *z*].

The crystal structure of **3** is shown in Fig. 3b. The octahedral $[Ni((CH_3)_2SO)_6]^{2+}$ complex has an average Ni–O bond distance of 2.06(2) Å, ranging from 2.041(3) to 2.085(3) Å. The mean S–O distance and Ni–S–O angle are 1.48(5) Å and 119(2)°, respectively. Complex **4** is essentially iso-structural with the chloride analogue, with the unit cell volume increased from 916.4(3) to 949.8(9) Å^3. The average Ni–O and O–S distances are 2.08(2) and 1.51(2) Å, respectively.

The crystal structure of **5** is shown in Fig. 3c. The octahedral $[Ni((CH_3)_2SO)_6]^{2+}$ cations have an average Ni–O distance of 2.07(1) Å, ranging from 2.059(3) to 2.079(3) Å. The average S–O bond distance and Ni–S–O angle are 1.517(6) Å and 117.8(1.4)°, respectively. The $NiCl_4^{2-}$ anions are found in two crystallographic environments. Ni3 has a tetrahedral geometry with a Ni–Cl distance of 2.2513(16) Å for the four symmetry equivalent Ni–Cl bonds. Ni2 lies on a four-fold axis giving a square pyramidal geometry. The four symmetry equivalent Cl atoms in the basal plane have an occupancy of 0.75 with a Ni–Cl distance of 2.229(3) Å whereas the Cl atom in the apex position has a Ni–Cl distance of 2.352(4) Å.

Vibration spectroscopy

The infrared and Raman spectra of the solids crystallographically characterized in this study are shown in Fig. S4.

Discussion

Complex formation is dependent on the bonding characteristics of the species forming a complex. The hard–soft acid–base (HSAB) principle gives a general view of the species expected to be formed and their relative stability based on the bonding characteristics of the metal ions and the donor atoms.[25] The solvating properties of the solvent plays an important role for the stability of the complex, as discussed in the Introduction. This study will focus on another factor scarcely discussed before, the influence of steric restrictions of the metal ion solvate.

In this study the complex formation of the nickel(II) bromide system has been studied in the two oxygen donor solvents dimethyl sulfoxide and *N*,*N*′-dimethylpropyleneurea. Both solvents are solvating the bromide ion fairly equally.[18] The D_S values of dimethyl sulfoxide and *N*,*N*′-dimethylpropyleneurea, 27.5 and 34, respectively,[18,26] show that *N*,*N*′-dimethylpropyleneurea is a somewhat stronger electron-pair donor, and it can be expected that it should solvate the nickel(II) ion at least as strongly as dimethyl sulfoxide. The major difference is that the nickel(II) ion is six-coordinated in an octahedral fashion in dimethyl sulfoxide solution, while it is five-coordinated, most probably in square-pyramidal fashion, in *N*,*N*′-dimethylpropyleneurea.[17] The present complex formation study shows that nickel(II) is not forming any complexes with bromide and iodide ions in dilute dimethyl sulfoxide solution, and the precipitation of **4** from saturated nickel(II) bromide solutions shows complex formation does not take place in concentrated solutions. Previous studies have shown that a relatively weak inner-sphere monochloronickel(II) complex is formed in dimethyl sulfoxide solution.[9–11] Precipitation of nickel(II) chloride from a dimethyl sulfoxide solution results in **5**, which gradually transforms to **3**.

An increase in the concentration, thus a decrease in the number of solvent molecules per solute, almost always results in formation of the most enthalpy stabilised complexes,[19] in this case the hexakis(dimethyl sulfoxide)nickel(II) solvate, and the highest chloro nickel(II) complex, tetrachloronickelate(II), and finally to the chloride salt.

Considering the HSAB properties of nickel(II) and bromide, and the solvating properties of dimethyl sulfoxide and *N*,*N*′-dimethylpropyleneurea complex formation is not expected in the latter solvent. However, the present study shows that two stable mononuclear complexes are formed in dilute solution, and that the solid precipitating from a concentrated *N*,*N*′-dimethylpropyleneurea solution of nickel(II) bromide contains bis(*N*,*N*′-dimethylpropyleneurea)dibromonickel(II) molecules (Fig. 3c). The reason for complex formation is most probably that the five-coordinated *N*,*N*′-dimethylpropyleneurea solvate is significantly less stable than the octahedral solvate complexes without crowding, and that a six-coordinated octahedral complex cannot be formed due to steric restrictions; the solvated pseudotetrahedral dibromo complex becomes the most stable one under these circumstances. Significant desolvation has already taken place on formation of the first complex, seen as a very positive entropy term (Table 2). Entropy stabilised complexes are normally not stable when the concentration increases and they rearrange to enthalpy stabilised ones,[19] in this case the solvated second complex.

Complex formation between nickel(II) and bromide has only been reported in the solvent *N*,*N*-dimethylacetamide, where somewhat weaker complexes than found in *N*,*N*′-dimethylpropyleneurea were reported.[14] The *N*,*N*-dimethylacetamide molecule is fairly bulky and therefore space demanding for solvation of metal ions, and it has been claimed that an equilibrium of the form: $\mathrm{Ni(dma)_6}^{2+} \rightleftharpoons \mathrm{Ni(dma)_4}^{2+} + 2\ \mathrm{DMA}$ exists.[27] This also shows that the hexakis(*N*,*N*-dimethylacetamide)nickel(II) solvate is labilized due to steric crowding, and that the formation of nickel(II) bromide complexes has the same background as in *N*,*N*′-dimethylpropyleneurea. These are examples of what we will call stereochemical induced reactivity.

Conclusions

Nickel(II) is a fairly hard electron-pair acceptor typically preferring to form complexes with hard ligands; the stability of the nickel(II) halide complexes decreases in the order $\mathrm{F^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$.[24] Nickel(II) forms fairly weak complexes with chloride ion in several solvents,[8–13] but significant complex formation with bromide ions has only been reported in *N*,*N*-dimethylacetamide[14] and in *N*,*N*′-dimethylpropyleneurea as shown in the present study. These two solvents have bulky structures which lead to a coordination number for the nickel(II) solvate of less than six and therefore lower stability of the solvate. In the presence of halide ions complex formation takes place where the driving force is the desolvation of a fairly labile solvate giving a large entropy term in *N*,*N*′-dimethylpropyleneurea. The most stable complex in this system is the bis-solvated second complex, which also precipitates from a concentrated *N*,*N*′-dimethylpropyleneurea solution (Fig. 3a). If the solvated nickel(II) ion is octahedral without any steric crowding and the solvation is sufficiently strong, as in dimethyl sulfoxide, weak complex formation with chloride ions is observed, but no complexes with bromide and iodide ions are formed, and the compounds precipitating from a concentrated nickel(II) halide solution are six-coordinated nickel(II) solvates with either halide or tetrahalonickelate(II) ions as counter ion. This shows that the five-coordinated solvate is more reactive than the six-coordinated one, and that stereochemically induced reactivity can be observed when labile solvates are formed due to steric restrictions.

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