Complexation of NpO_2^+ with *N*-methyl-iminodiacetic Acid: in Comparison with Iminodiacetic and Dipicolinic Acids

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Complexation of Np(V) with *N*-methyl-iminodiacetic acid (MIDA) in 1 M $NaClO_4$ solution was studied with multiple techniques including potentiometry, spectrophotometry, and microcalorimetry. The 1:2 complex, $NpO_2(MIDA)_2^{3-}$ was identified for the first time in aqueous solution. The correlation between its optical absorption properties and symmetry was discussed, in comparison with Np(V) complexes with two structurally related nitrilo-dicarboxylic acids, iminodiacetic acid (IDA) and dipicolinic acid (DPA). The order of the binding strength (DPA > MIDA > IDA) is explained by the difference in structural and electronic properties of the ligands. In general, the nitrilo-dicarboxylates form stronger complexes with Np(V) than oxy-dicarboxylates due to a much more favorable enthalpy of complexation.

Introduction

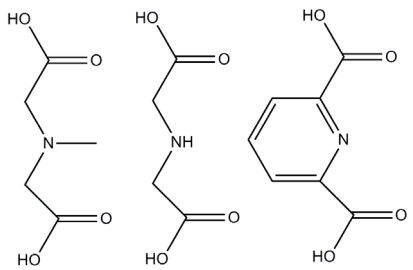
Neptunium is a "problematic" element in spent nuclear fuel reprocessing because it could exist in multiple oxidation states (e.g., IV, V and VI) and the most stable oxidation state, NpO_2^+, has very low extractability in solvent extraction separation processes due to its low ionic charge. In the development of advanced nuclear fuel cycles, there is an urgent need to search for ligands that could form strong complexes with NpO_2^+ and make it extractable in solvent extraction.

In recent years, a group of oxy- and nitrilo- dicarboxylic acids and their diamide derivatives have been the subject of study for the complexation of actinides. For the series of oxy-ligands from oxydiacetic acid (ODA), to *N,N*-dimethyl-3-oxa-glutarimic acid (DMOGA), and to *N,N,N',N'*-tetramethyl-3-oxa-glutaramide (TMOGA), thermodynamic data show that they all form moderately strong tridentate complexes with NpO_2^+, and that there are systematic changes in enthalpy and entropy of complexation when the carboxylate group is replaced with the amide group.[1,2] For the nitrilo ligands, iminodiacetic acid (IDA)[3,4] and dipicolinic acid (DPA)[5] form quite strong tridentate complexes with NpO_2^+. The amide derivatives of DPA have been shown to be effective for extracting actinides in various oxidation states.[6-8] These studies have helped with the development of effective extractants for actinide separations.

Besides providing help with the separation processes, the studies of the series of oxy- and nitrilo- dicarboxylic acids and their diamide derivatives have also revealed some fundamental properties of the Np(V) complexes. For example, the optical absorption properties of Np(V) complexes were experimentally shown to be closely related to the symmetry of the complexes.[2,4,5,9,10] The 1:2 Np(V) complexes with ODA,[9] TMOGA[2] and DPA[5] all have an inversion center (at the Np atom). The f-f transitions in these 1:2 Np(V) complexes are completely forbidden and no characteristic optical absorption bands in the near IR regions are observed for $NpO_2(ODA)_2^{3-}$, $NpO_2(TMOGA)_2^+$, or $NpO_2(DPA)_2^{3-}$. In contrast, though IDA ligand forms similar tridentate complexes with Np(V), its 1:2 Np(V) complex, $NpO_2(IDA)_2^{3-}$, does show characteristic absorption bands.[4] This observation was interpreted as the co-existence of trans- and cis- isomers, depending on the positions of the two imino-hydrogen atoms with respect to the equatorial plane of NpO_2^+. The energy difference between the two configurations is expected to be small. The *cis*-isomer, with the imino-hydrogen atoms on the same side of the plane, is obviously not centrosymmetric and should absorb in the near IR region. The *trans*- isomer of $NpO_2(IDA)_2^{3-}$ is centrosymmetric and does not absorb.[10]

Fig. 1 *N*-methyl-iminodiacetic acid (MIDA), iminodiacetic acid (IDA), and dipicolinic acid (DPA).

Substitution of the imino hydrogens in IDA with the methyl groups in *N*-methyl-iminodiacetic acid (MIDA, Fig.1) could have significant consequence in the symmetry of the 1:2



MIDA IDA DPA

Np(V) complexes with MIDA. A *cis*- isomer of $NpO_2(MIDA)_2^{3-}$ with the two methyl groups on the same side of the equatorial plane is less likely to form, because the steric hindrance in the *cis*-configuration of $NpO_2(MIDA)_2^{3-}$ is large so that the energy of the *cis*- isomer is significantly higher than the *trans*- isomer. In fact, a crystal structure of $NpO_2(MIDA)_2^{3-}$ with the methyl groups *trans*- to the equatorial plane of NpO_2^+ was identified,[11] but no cis-structure of $NpO_2(MIDA)_2^{3-}$ has been found.

Though MIDA is expected to form similar tridentate 1:1 and 1:2 complexes with Np(V) in aqueous solutions as IDA and DPA, only the 1:1 complex, $NpO_2(MIDA)^-$, has been observed in previous studies.[12,13] We hypothesize that the 1:2

complex, $NpO_2(MIDA)_2^{3-}$, should also form in aqueous solution and that it possesses an inversion center so that it might have been "missed" in the previous study by spectrophotometry[12] due to its "silence" in the near IR absorption spectra.

To reveal the thermodynamic principle and structural factors governing the coordination chemistry of Np(V) and help to improve the efficiency of Np(V) in separation processes, we have studied the complexation of Np(V) with MIDA in aqueous solutions in this work, in comparison with IDA and DPA. For the first time, spectrophotometric titrations have shown that $NpO_2(MIDA)_2^{3-}$ forms in solution but does not absorb in the near IR region, suggesting a centrosymmetric structure in solution. Thermodynamic parameters ($\log\beta$, ΔH and ΔS) of $NpO_2(MIDA)^-$ and $NpO_2(MIDA)_2^{3-}$ were determined by a combination of potentiometry, spectrophotometry and microcalorimetry. To compare with the Np(V)/IDA system, new data on the stability constants (by potentiometry) and enthalpy (by microcalorimetry) of $NpO_2(IDA)^-$ and $NpO_2(IDA)_2^{3-}$ have also been obtained and included in this paper.

Experimental

Chemicals

All chemicals were reagent-grade or higher. Boiled/cooled Milli-Q water was used in preparation of all solutions. All experiments were conducted at 25 °C and an ionic strength of 1.0 M ($NaClO_4$). The stock solution of Np(V) in perchloric acid was prepared as described elsewhere.[14] The concentration of Np(V) was determined by the absorbance at 980.2 nm (ε = 395 $M^{-1}\cdot cm^{-1}$). The concentration of perchloric acid in the stock solution was determined by Gran's titration.[15] *N*-methyliminodiacetic acid (MIDA, 99%) and iminodiacetic acid (IDA, 98%, Aldrich) were used as received. Buffered MIDA and IDA solutions were prepared by neutralizing weighted acids with a standard NaOH solution (0.999 ± 0.00196 M, Brinkmann) and diluting to appropriate concentrations.

Potentiometry

The electrode potential (*E*, in millivolts) was measured with a Metrohm pH meter (Model 713) equipped with a Ross combination pH electrode (Orion Model 8102) under inert atmosphere (Ar). The original inner solution (3 M KCl) of the electrode was replaced with 1 M NaCl to reduce the electrode junction potential. Prior to each titration, an acid-base titration with standard $HClO_4$ and NaOH solutions was performed to obtain the electrode parameters which allowed the calculation of hydrogen ion concentrations from the electrode potential in the following titration. Multiple titrations were conducted with solutions of different concentrations of Np(V) (C_{Np} for total Np(V)), MIDA or IDA (C_L for total ligand), and different acidity (C_H for total hydrogen ion). For determining the protonation constant of MIDA, 20 mL of MIDA solutions (C_L: 0.02–0.025 M; C_H: 0.04–0.08 M) were titrated with 0.1 M NaOH solution, and 100 – 200 data points were collected in each titration. For determining the stability constants of the Np(V)/MIDA and Np(V)/IDA complexes, 6 mL of Np(V) solutions (C_{Np}: 1.00 – 2.00 mM; C_H: 1.21 – 2.42 mM) were titrated with 0.020 – 0.050 M Na_2(MIDA) or Na_2(IDA) solutions, and about 40 – 50 data points were collected for each titration. The protonation constants of MIDA and the stability constants of Np(V)/MIDA and Np(V)/IDA complexes were calculated using the nonlinear regression program Hyperquad 2006.[16]

Spectrophotometry

Spectrophotometric titrations of Np(V) were carried out on a Cary 6000i spectrophotometer (Varian Inc.) from 1150 to 950 nm with an interval of 0.1 nm. The Np(V) solution (2.5 mL) was put in a 1 cm cuvette and titrated with buffered MIDA solutions. After each addition of the titrant, the solution was mixed thoroughly (for 1 – 2 minutes) before the spectrum was collected. Preliminary kinetic experiments showed that the complexation reaction was fast, and the absorbance became stable within 30 seconds of mixing. Usually, 15 – 20 additions were made, generating a set of 16 – 21 spectra in each titration. Multiple titrations with different concentrations of Np(V) were performed. The formation constants of Np(V)/MIDA complexes were calculated by Hyperquad 2006.

Microcalorimetry

Calorimetric titrations were conducted at 25 °C with an isothermal microcalorimeter (Model: ITC 4200, Calorimetry Sciences Corp.). Procedures and results of the calibration of the calorimeter were provided elsewhere.[17] Three titrations with different concentrations of Np(V) (1.0 – 2.5 mM) were performed to reduce the uncertainty of the results. In each titration, 0.9 mL of Np(V) solution was put in the reaction cell, and *n* additions of 0.005 mL of the titrant (MIDA or IDA) were made (n = 40 – 50) through a 0.250 mL syringe, resulting in *n* experimental values of total heat ($Q_{ex,j}$, j = 1 to n). These values were corrected for the heats of titrant dilution ($Q_{dil,j}$) that were measured in a separate run. The net reaction heat at the *j*th point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The value of $Q_{r,j}$ is a function of the concentrations of the reactants (C_{Np}, C_H, and C_L), the equilibrium constants, and the enthalpies of the reactions that occurred in the titration. These data, in conjunction with the protonation constants obtained by potentiometry, the stability constants of Np(V)/MIDA and Np(V)/IDA obtained by potentiometry and/or spectrophotometry, and the enthalpy of protonation of MIDA and IDA determined in separate microcalorimetric titrations, were used to calculate the enthalpy of compexation for Np(V)/MIDA and Np(V)/IDA complexes with the computer program Letagrop.[18]

Results and Discussion

Equilibrium constants and enthalpy of protonation of MIDA

MIDA has three protonation sites: the amino nitrogen and the two carboxylate oxygens. The overall protonation constants and entahlpy of protonation determined in this work are shown in Table 1. The protonation constants are consistent with those at other ionic strengths in the literature.[19] The enthalpies of protonation, ΔH_1 for ($H^+ + MIDA^{2-} = H(MIDA)^-$) and ΔH_2 for ($2H^+ + MIDA^{2-} = H_2(MIDA)(aq)$), are the first such values directly determined by microcalorimetry. The enthalpy of the third protonation reaction, ΔH_3 for ($3H^+ + MIDA^{2-} = H_3(MIDA)^+$) was not determined in this work, because this reaction only occurs in strongly acidic solutions and the value of ΔH_3 is not needed in the calculation of the enthalpy of Np(V)/MIDA complexation under the conditions in this work.

Stability constants of Np(V)/MIDA and Np(V)/IDA complexes by potentiometry

Fig. 2 shows representative potentiometric titrations of Np(V) with MIDA and IDA. The best fit of the titration data indicates that two successive complexes (1:1 and 1:2) formed during the titration. The calculated stability constants are summarized in Table 1.

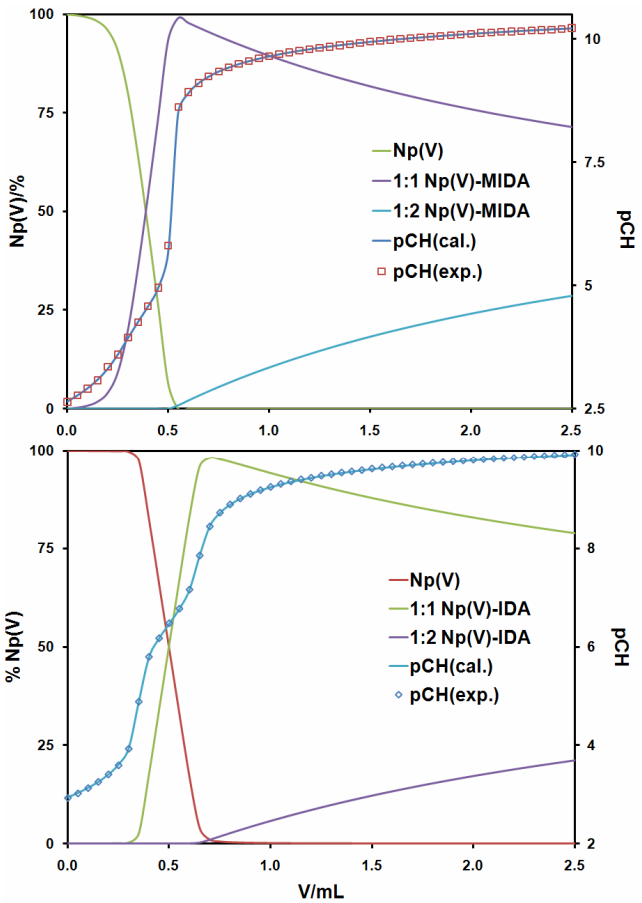


Fig. 2 Potentiometric titrations of Np(V) complexation with MIDA and IDA (t = 25 °C, I = 1.0 M $NaClO_4$). (top) Np(V)/MIDA: V_0 = 6 mL, C_{Np}^0 = 2.03 mM, C_H^0 = 2.30 mM, titrant - 0.050 M Na_2MIDA. (bottom) Np(V)/IDA: V_0 = 6.00 mL, C_{Np}^0 = 1.01 mM, C_H^0 = 1.16 mM, titrant - 0.020 M Na_2IDA. Right y-axis: pC_H (= -log[H^+]); left y-axis: % of Np(V) species.

The stability constant of the 1:1 complex, $NpO_2(MIDA)^-$, ($\log\beta_1$ = 7.36 at I = 1 M) is consistent with the values at other ionic strengths in the literature. The stability constant of the 1:2 complex, $NpO_2(MIDA)_2^{3-}$, is the first data available. This complex has not been identified in previous studies.

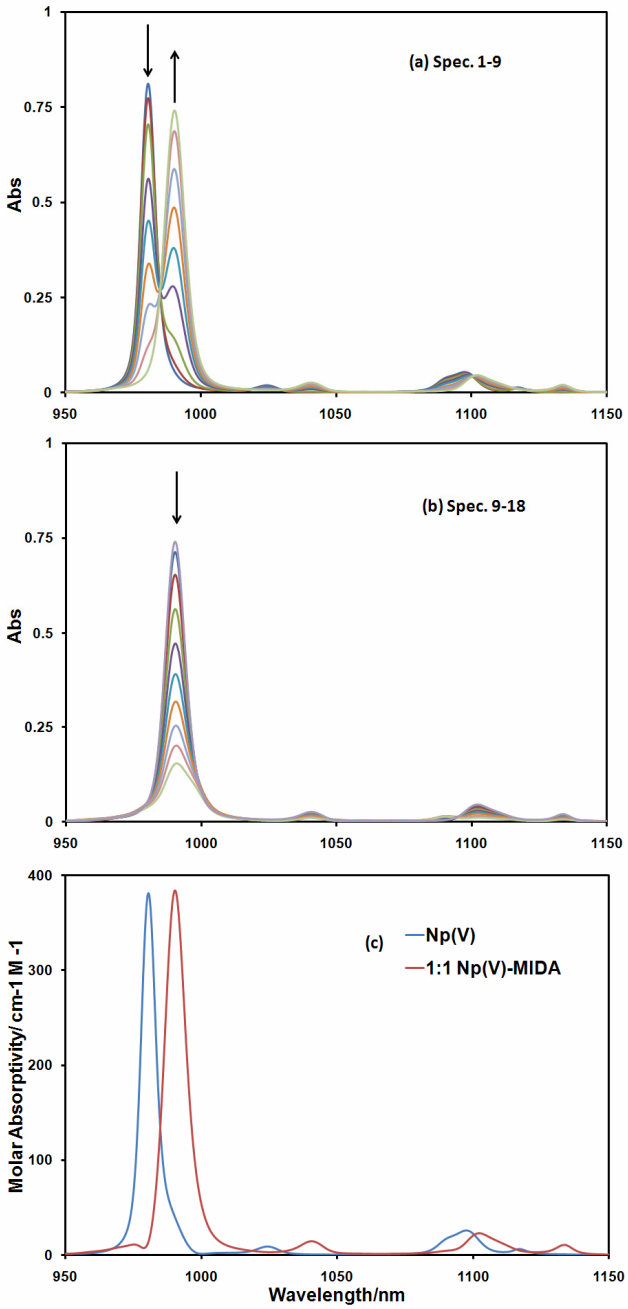


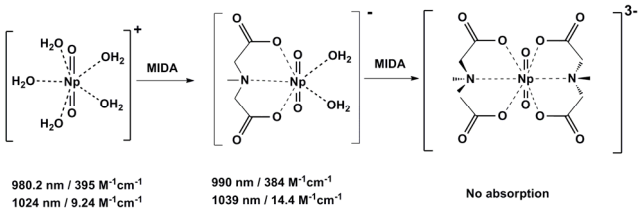
Fig. 3 Spectrophotometric titration of NpO_2^+ with MIDA (t = 25 °C, I = 1.0 M $NaClO_4$). Cell solution: V^0 = 2.50 mL, C_{Np}^0 = 2.05 mM, C_H^0 = 2.37 mM. Titrant: 0.200 M Na_2MIDA, 1.465 mL (total) added. The 18 spectra shown are not normalized in terms of C_{Np}^0. (a) Phase I: spectra 1 – 9 ($C_{MIDA}/(C_{Np}+C_H) \approx 0 - 1$); (b) Phase II: spectra 9 - 18 ($C_{DPA}/(C_{Np}+C_H) > 1$); (c) calculated absorptivities of NpO_2^+ (blue) and $NpO_2(MIDA)^-$ (red).

The stability constants of the 1:1 and 1:2 Np(V)/IDA complexes determined by potentiometry in this work are in good agreement with the previous values[4] obtained by spectrophotometry (Table 1).

Stability constants of Np(V)/MIDA complexes by spectrophotometry and the correlation between optical absorption property and symmetry

Fig. 3 shows a representative set of absorption spectra in the near IR region for the titration of Np(V) with MIDA. The variation in the spectra of Np(V) during the titration can be described with two phases, I and II. In phase I (Fig. 3a), as MIDA was added, the intensities of the absorption bands at 980, 1024 nm that belong to the free NpO_2^+ decreased, while new bands appeared at longer wavelengths (990, 1039 nm), indicating the formation of a new Np(V) species. The new bands were assigned to the $NpO_2(MIDA)^-$ complex, because the band positions agree with those of the 1:1 complex previously observed with ODA and IDA. In phase II (Fig. 3b), as the concentration of MIDA was further increased, the intensities of these bands gradually decreased, but no new absorption bands appeared. The variation of spectra in the titration of Np(V)/MIDA is very similar to those observed in the complexation of Np(V) with ODA,[9] DPA,[5] and TMOGA,[2] suggesting that two Np(V)/MIDA complexes formed successively during the titration, but the second complex, $NpO_2(MIDA)_2^{3-}$, did not absorb in the near IR region. Factor analysis with Hyperquad also indicates that there are only two absorbing Np(V) species (the free NpO_2^+ and the 1:1 complex). Based on this analysis, the stability constants and molar absorptivity (Fig. 3c) of the complexes were calculated.

The relationship between the optical properties and the structure of the 1:2 Np(V) complexes with ODA, DPA and TMOGA has been discussed previously.[10] Because these complexes are centrosymmetric with the Np atom at the inversion center, the f-f transitions are forbidden and they do not absorb in the near IR region. The spectrophotometric data on Np(V)/MIDA from this work indicate that $NpO_2(MIDA)_2^{3-}$ in solution is also centrosymmetric, consistent with the observed structure in the crystal form.[11] The correlation between the optical absorption properties and the structures of the Np(V)/MIDA complexes in the spectrophotometric titration is best illustrated in Scheme I.



Scheme I

It is interesting to compare the structures and optical properties of the 1:2 Np(V) complexes with the three nitrilo-dicarboxylic acids (DPA, IDA and MIDA, Fig.1). In the DPA complex, $NpO_2(DPA)_2^{3-}$, two DPA ligands coordinate to Np perfectly in the equatorial plane of NpO_2^+, with a D_{2h} symmetry. In the IDA complex, $NpO_2(IDA)_2^{3-}$, the two imino-hydrogen atoms are out of the equatorial plane and can be cis- or trans- with respect to the plane. The cis-isomer has no inversion center and absorbs in the near IR region, but the tran-isomer is silent in optical absorption due to the existence of an inversion center. The energy difference between the cis- and trans-isomers of $NpO_2(IDA)_2^{3-}$ is expected to be insignificant because the hydrogen atom is small, resulting in the coexistence of cis- and trans- isomers of $NpO_2(IDA)_2^{3-}$ in solution. Therefore, absorption bands of $NpO_2(IDA)_2^{3-}$ with somewhat lower intensity are observed at 993 nm.[4,10]

The $NpO_2(MIDA)_2^{3-}$ complex can also have cis- and trans-isomers, with the two methyl groups at the same or opposite sides of the equatorial plane. However, the energy difference between the two isomers is expected to be significantly larger than that in $NpO_2(IDA)_2^{3-}$. The energy of the trans- isomer should be lower due to less steric strain. As a result, only the trans- isomer forms in solution and no optical absorption is observed because it is centrosymmetric with the Np at the inversion center.

Enthalpy of complexation for Np(V)/MIDA and Np(V)/IDA complexes

Fig. 4 shows representative sets of calorimetric titration of Np(V) with MIDA and IDA. With the information on the speciation of Np(V) during the titration, the titration thermograms could be described as three stages. Stage I was highly exothermic and the major contribution to the heat released was from the protonation of the ligands. For the titration with IDA (left), Stage I consisted of only the first addition because little free acid (0.01 mM) was in the initial cell solution and was consumed by the IDA in the first addition. For the titration with MIDA (right), Stage I was longer (5 additions) because there was more free acid in the initial cell solution (1.93 mM). Integration of the peaks on the plateau of Stage I should result in the protonation enthalpy of MIDA. In both titrations, Stage II and III correspond to the formation of the 1:1 and 1:2 complexes, respectively. The titration thermograms indicate that the formation of 1:1 complex, $NpO_2(IDA)^-$ and $NpO_2(MIDA)^-$, are highly exothermic, but the formation of 1:2 complex, $NpO_2(IDA)_2^{3-}$ and $NpO_2(MIDA)_2^{3-}$, are only slightly exothermic,

The calculated enthalpy and entropy of complexation are listed in Table 1.

Thermodynamic trends

In general, all three nitrilo- dicarboxylic acids (MIDA, IDA DPA) form much stronger complexes with Np(V) than the oxy-dicaboxylic acids (e.g., ODA) and corresponding oxy-diamides (e.g., TMOGA). In comparison, coordination by the nitrilo- ligands is much more favored by enthalpy than the coordination by the oxy- ligands. For example, ΔH is -30 to -50 kJ/M for the 1:1 Np(V) complexes with nitrilo-dicarboxylic acids (Table 1), but +8.7 kJ/M for the 1:1 Np(V)/ODA complex.[9] Probably the nitrogen atom is much less hydrated than the oxygen so that less de-hydration energy is required when forming the Np(V)/nitrilo-dicarboxylate complexes. Corresponding diamide derivatives of MIDA, IDA and DPA, i.e., *N*-methyl-iminodiamide, iminodiamide and dipicolinamide, could have important applications in separating neptunium due to two reasons: (1) they all are expected to coordinate with Np(V) strongly as their nitrilo-dicarboxylate analogs, and (2) the amide moiety allows the

attachment of big akyl- and/or aryl- groups so that they can be used as extractants in solvent extraction.

In the series of the three nitrilo- dicarboxylic acids, the stability constants of Np(V) complexes follow the order: DPA > MIDA > IDA (see Table 1). The high strength of Np(V)/DPA complexes could be rationalized by the "rigid" and conjugated structure of DPA in which the pyridine nitrogen and two carboxylate groups are arranged at optimal positions to coordinate with NpO_2^+ in its equatorial plane. Therefore, little energy for ligand reorganization is required to form the Np(V)/DPA complexes. On the other hand, the electron donating ability of the methyl group in MIDA increases the electron density on the nitrogen, making MIDA a stronger ligand than IDA.

Conclusions

N-methyl-iminodiacetic acid (MIDA) forms strong complexes with NpO_2^+, as the other nitrilo- dicarboxylic acids (IDA and DPA). The 1:2 complex, $NpO_2(MIDA)_2^{3-}$, has been identified in aqueous solution for the first time and the stability constant calculated by optical absorption spectroscopy as well as potentiometry. The optical absorption properties of $NpO_2(MIDA)_2^{3-}$ are consistent with a centrosymmetric structure in which the two methyl groups are trans- with respect to the equatorial plane of NpO_2^+. In contrast to the complexation of Np(V) with oxy- dicarboxylates where the complexation is not favored by enthalpy, the complexation of Np(V) with all three nitrilo- dicarboxylic aicds (MIDA, IDA and DPA) is highly favored by enthalpy, because less dehydration energy is required when forming the Np(V)/nitrilo- dicarboxylate complexes.

Acknowledgments

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Notes and references

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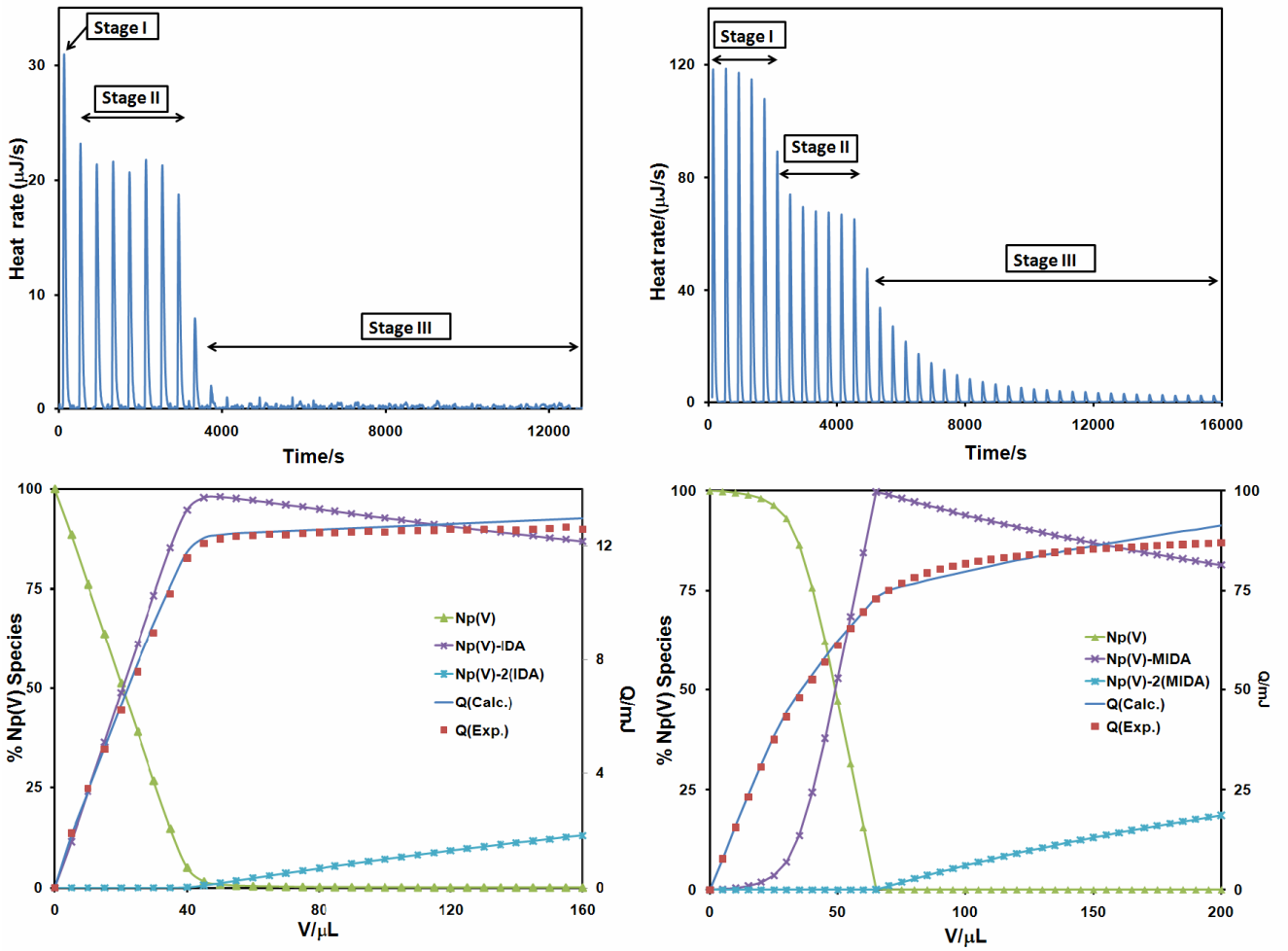

Fig. 4 Calorimetric titrations of the complexation of Np(V) with IDA and MIDA (t = 25 °C, I = 1.0 M $NaClO_4$). Upper figures: titration thermogram; lower figures: accumulative reaction heat (right y-axis) and speciation of Np(V) (left y-axis) *vs*. the volume of titrant. Left figures: Np(V)/IDA; V^0 = 0.900 ml, C_H^0 = 0.01 mM, $C_{Np(V)}^0$ = 1 mM; titrant C_{IDA}/C_H = 0.025/0.0025 M, 0.005 mL × 34 additions. Right figures: Np(V)/MIDA; V^0 = 0.900 ml, C_H^0 = 1.93 mM, $C_{Np(V)}^0$ = 1.67 mM; titrant C_{MIDA} = 0.050 M, 0.005 mL × 40 additions.

Table 1 Thermodynamic parameters of the complexation of NpO_2^+ with MIDA and related ligands (t = 25 °C), pot – potentiometry, sp – spectrophotometry, cal – calorimetry, ix – ion exchange, p.w. – present work.

Reaction	I, M	Method	Log K	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, J/(K·mol)	Ref.
$H^+ + MIDA^{2-} = H(MIDA)^-$	1.0	pot,cal	9.45 ± 0.03	-54.95 ± 0.2	-32.7 ± 1.4	74.6 ± 4.8	p.w.
$2H^+ + MIDA^{2-} = H_2(MIDA)$ (aq)	1.0	pot,cal	11.8 ± 0.1	-67.36 ± 0.6	-31.6 ± 2.1	119.9 ± 7.3	p.w.
$3H^+ + MIDA^{2-} = H_3(MIDA)^+$	1.0	pot,cal	13.3 ± 0.3				p.w.
$NpO_2^+ + MIDA^{2-} = NpO_2(MIDA)^-$	1.0	sp,cal	7.36 ± 0.12	-42.0 ± 0.7	-16.8 ± 2.1	84.6 ± 7.1	p.w.
		pot	7.45 ± 0.15				
	0.1	ix	7.37				13
	0.5	sp	6.75 ± 0.03				12
$NpO_2^+ + 2MIDA^{2-} = NpO_2(MIDA)_2^{3-}$	1.0	sp,cal	8.96 ± 0.22	-51.1 ± 1.2	-22.2 ± 2.4	96.9 ± 9.0	p.w.
		pot	9.04 ± 0.24				
$NpO_2^+ + IDA^{2-} = NpO_2(IDA)^-$	1.0	pot,cal	5.85 ± 0.22	-33.4 ± 0.7	-13.5 ± 1.8	66.7 ± 6.5	p.w.
	1.0	sp,pot,cal	5.88 ± 0.01	-33.57 ± 0.06	-16.0 ± 0.2	58.9 ± 0.7	3
	1.0	sp	5.80 ± 0.04				4
$NpO_2^+ + 2IDA^{2-} = NpO_2(IDA)_2^{3-}$	1.0	pot,cal	7.62 ± 0.22	-43.5 ± 0.9	-16.2 ± 2.6	91.6 ± 9.2	p.w.
	1.0	sp	7.62 ± 0.04				4
$NpO_2^+ + DPA^{2-} = NpO_2(DPA)^-$	1.0	sp,cal	8.68 ± 0.11	-49.6 ± 0.6	-25.2 ± 0.7	81.6 ± 2.5	12
$NpO_2^+ + 2DPA^{2-} = NpO_2(DPA)_2^{3-}$	1.0	sp,cal	11.31 ± 0.11	-64.6 ± 0.6	-45.9 ± 1.4	81.8 ± 5.5	12