Symmetry and optical spectra: a "silent" 1 : 2 Np(V)–oxydiacetate complex

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The 1 : 2 Np(V)–oxydiacetate complex, $NpO_2(ODA)_2^{3-}$, identified by single-crystal X-ray diffractometry for the first time, is centrosymmetric around the Np atom so that the f–f transitions of Np(V) are forbidden, resulting in the "silence" of the absorption and diffuse reflectance spectra of this complex in solution and the solid state in the near-IR and visible regions.

The relationship between the symmetry of NpO_2^+ species and the intensity of its absorption spectra has been extensively studied by Krot *et al.*[1] The absorption bands of NpO_2^+ in the near IR and visible region originate from f–f transitions[2] so that they are electric-dipole forbidden by Laporte's rule.[3] The intense characteristic band at 980 nm is observed only if the arrangement of ligands around NpO_2^+ does not contain a center of inversion. If the complex is centrosymmetric and the neptunium atom is at the inversion center, the f–f transitions of neptunium are completely forbidden and this band will be "silent". The "silent" features of the absorption spectra of centrosymmetric Np(V) species have been observed for a Np(V) complex with triphenylphosphine oxide in crystal[4] and the $NpO_2(OH)_x^{(x-1)-}$ species (x = 2 or 4) in solution.[5,6] Recently, the optical properties and crystal structure of a centrosymmetric Np(V) complex with *N*,*N*,*N*′,*N*′-tetramethyl-3-oxaglutaramide (TMOGA, Fig. 1) have been characterized.[7] The structure of the complex has helped to interpret the data from the spectrophotometric titration of Np(V) with TMOGA and confirmed the formation of both 1 : 1 and 1 : 2 Np(V)–TMOGA complexes in solution.[7]

Oxydiacetic acid (ODA, Fig. 1) and TMOGA are chemical analogs and are expected to form complexes with similar stoichiometry and structure. However, no crystal structures of Np(V) complexes with ODA have been reported in the literature. Furthermore, previous spectrophotometric titrations of Np(V)–ODA suggest that Np(V) forms only the 1 : 1 complex with ODA.[8,9] No evidence has been found for the formation of the 1 : 2 Np(V)–ODA complex in solution or solid. Taking into consideration the similarity in the structures of ODA and TMOGA, as well as the fact that the ODA complexes with actinyl cations (*e.g.*, UO_2^{2+}) are usually stronger than the TMOGA complexes in aqueous solutions,[10] the absence of the 1 : 2 Np(V)–ODA complex is surprising. Accordingly, we hypothesized that the 1 : 2 Np(V)–ODA complex may in fact exist, but has been "missed" because it may possess an inversion center so that it does not have observable absorption bands in the near-IR and visible regions due to the same selection rule for the f–f transitions previously mentioned. In this work, experimental studies were conducted to test this hypothesis with multiple techniques including optical absorption spectroscopy, diffuse reflectance spectroscopy and X-ray single-crystal diffractometry.

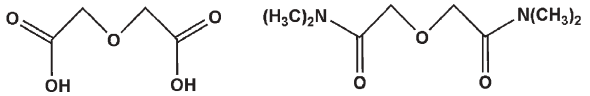

Fig. 1 Oxydiacetic acid (ODA, left) and *N*,*N*,*N*′,*N*′-tetramethyl-3-oxaglutaramide (TMOGA, right).

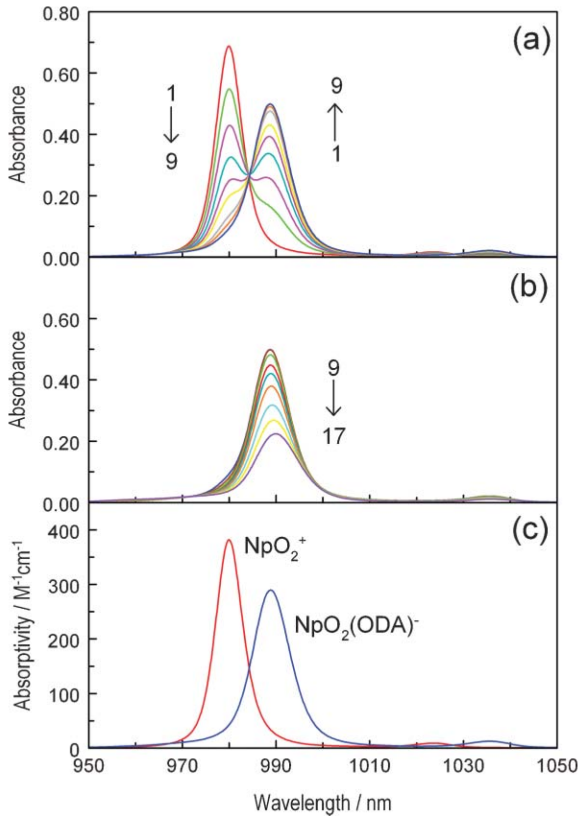

Fig. 2 (a, b) Spectrophotometric titrations of NpO_2^+ with ODA: T = 25 °C. Initial solution (1.0 M $NaClO_4$): $V°$ = 2.50 mL, $C_{Np}°$ = 1.78 mM, pH = 6; Titrant: 1.0 M Na_2ODA, a total of 2.50 mL added. Optical path = 1.0 cm. The 17 spectra shown are normalized in terms of $C_{Np}°$ for clarity. (c) Deconvoluted spectra of NpO_2^+ and the 1 : 1 $NpO_2(ODA)^-$ complex. The 1 : 2 $NpO_2(ODA)_2^{3-}$ complex does not absorb.

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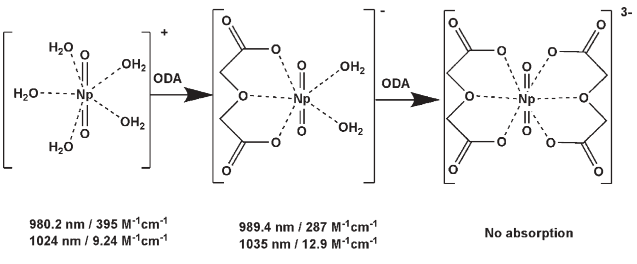
Fig. 2 shows the spectrophotometric titrations of NpO_2^+ with ODA in the near IR region. As the concentration of ODA was increased, the intensities of the absorption bands at 980 and 1024 nm that belong to the free NpO_2^+ cation decreased, while new bands appeared at 989 and 1035 nm and their intensities increased, corresponding to the formation of a 1 : 1 $NpO_2(ODA)^-$ complex (Fig. 2(a)). As the concentration of ODA was further increased, the intensities at 989 and 1035 nm started to decrease but no new absorption peaks appeared at longer wavelengths (Fig. 2(b)). These changes in the spectra are different from those for NpO_2^+ complexation with many other ligands (*e.g.*, oxalate) where the decrease of the absorbance of the first complex is accompanied by the appearance of new absorption band(s) of successive complexes at longer wavelengths.

The variation of spectra in Fig. 2 is very similar to that observed in the spectrophotometric titrations of Np(V) with TMOGA[7] and can be interpreted with the assumption that two complexes of NpO_2^+ with ODA formed in solution successively but the second complex, $NpO_2(ODA)_2^{3-}$, did not absorb in the wavelength region. Factor analysis of the spectra by the Hyperquad 2000 program[11] indicates that there are only two absorbing species (NpO_2^+ and $NpO_2(ODA)^-$), supporting this assumption. Using Hyperquad 2000, deconvoluted spectra for NpO_2^+ and $NpO_2(ODA)^-$ are obtained (Fig. 2(c)). The formation constants of the 1 : 1 $NpO_2(ODA)^-$ and 1 : 2 $NpO_2(ODA)_2^{3-}$ complexes are calculated to be: $\log \beta_1 = 3.89 \pm 0.05$ and $\log \beta_2 = 4.40 \pm 0.05$, respectively, at $I = 1.0$ M Na(ClO_4/ODA) and $T = 25$ °C. The value of $\log \beta_1$ is in good agreement with previous results in the literature, 3.72 ($I = 0.5$ M $NaClO_4$)[8] and 3.87 ($I = 1.0$ M $NaClO_4$).[9] Previous studies did not observe the formation of the 1 : 2 complexes because the concentrations of ODA were insufficient and, probably, because the non-absorbing nature of the $NpO_2(ODA)_2^{3-}$ complex was not recognized.

If the $NpO_2(ODA)_2^{3-}$ complex is centrosymmetric as the $NpO_2(TMOGA)_2^+$,[7] the results of spectrophotometric titrations in Fig. 2 can be well interpreted by the theoretical calculations of Pitzer and co-workers[2] Their calculations have shown that, for the $5f^2$ electronic configuration of Np(V), the f–f transitions are forbidden if the Np(V) species possess an inversion center (*e.g.*, in $NpO_2(ODA)_2^{3-}$). The f–f transitions become allowed only if the coordinating ligands are arranged so that the inversion center is destroyed (*e.g.*, in $NpO_2(H_2O)_5^+$ and $NpO_2(ODA)^-$). The successive formation of the 1 : 1 and 1 : 2 NpO_2^+–ODA complexes and the accompanying changes in symmetry and absorption spectra are best illustrated by Scheme 1.

If the $NpO_2(ODA)_2^{3-}$ complex is centrosymmetric, it should not have absorption bands in the visible region, either, because the theoretical calculations also indicate that the absorption bands of Np(V) in the visible region (up to 23000 cm^{-1}) all originate from f–f transitions and thus follow Laporte's rule.[2] Indeed, the experimental spectra of the Np(V)–ODA solutions in the region from 400 to 800 nm showed that the sharp and weak absorption bands that belong to the non-centrosymmetric $NpO_2(H_2O)_5^+$ and $NpO_2(ODA)^-$ species decreased as the $NpO_2(ODA)_2^{3-}$ complex forms, in the same manner as for the Np(V)–TMOGA system reported previously.[7]



Scheme 1

To prove the hypothesis that the 1 : 2 $NpO_2(ODA)_2^{3-}$ complex is centrosymmetric, single crystals of a Np(V)–ODA complex were prepared from an aqueous solution containing 0.05 M NpO_2ClO_4 and 0.4 M ODA in 1 M $NaClO_4$ (pH 5–7) by slow evaporation. Single crystal X-ray diffraction data were collected on the Small Molecule X-ray Crystallography Beamline (11.3.1) at the Advanced Light Source (ALS).[12] The structure of the $NpO_2(ODA)_2^{3-}$ moiety in the crystal is shown in Fig. 3.

The unit cell contains one NpO_2^+ moiety, two ODA ligands, two water molecules and three sodium atoms, as $Na_3NpO_2(ODA)_2 \cdot 2H_2O$ crystallized in the primitive, centric triclinic space group $P\bar{1}$. The Np atom is located on the inversion center at [0.5, 0.5, 0.5]. The Na atoms are not shown in Fig. 3, but one Na atom also lies on an inversion center at [1.0, 0.5, 1.0]. The O=Np=O moiety is linear and symmetrical, with an angle of 180° and Np=O distance of 1.841 Å. It is coordinated equatorially by three oxygens of each of the two coplanar ODA ligands (Fig. 3). The bond distances between Np and the two carboxylate oxygens are slightly different, $R_{Np1-O1} = 2.543$ Å and $R_{Np1-O4} = 2.577$ Å, probably due to the interactions between the sodium and one carboxylate group in the crystal. As a result, the $NpO_2(ODA)_2^{3-}$ moiety in the $Na_3NpO_2(ODA)_2 \cdot 2H_2O$ molecule (Fig. 3) has lower symmetry than $NpO_2(TMOGA)_2^+$ where Np is located at the cross point of three mirror planes perpendicular to each other.[7] However, in either $Na_3NpO_2(ODA)_2 \cdot 2H_2O$ or $NpO_2(TMOGA)_2^+$, Np is located at an inversion center.

The $Na_3NpO_2(ODA)_2 \cdot 2H_2O$ compound dissociates in aqueous solution to generate Na^+ and the anionic $NpO_2(ODA)_2^{3-}$ complex. It is very likely that the inversion center in the $Na_3NpO_2(ODA)_2 \cdot 2H_2O$ solid will be maintained in the $NpO_2(ODA)_2^{3-}$ anion in solution. In fact, the latter could have higher symmetry than the $NpO_2(ODA)_2^{3-}$ moiety in the solid, because of the absence of crystal lattice constraints in solution. In particular, the absence of specific interactions between the sodium and one carboxylate oxygen could make the Np1–O1 and Np1–O4 bonds of $NpO_2(ODA)_2^{3-}$ identical in solution.

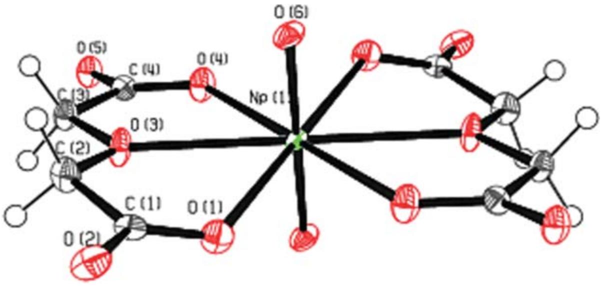


Fig. 3 Structure of the $NpO_2(ODA)_2^{3-}$ moiety in the single crystal of $Na_3NpO_2(ODA)_2 \cdot 2H_2O$ (50% probability ellipsoids). The sodium atoms and water molecules are not shown for clarity. Np – green, O – red, C – grey, H – white.

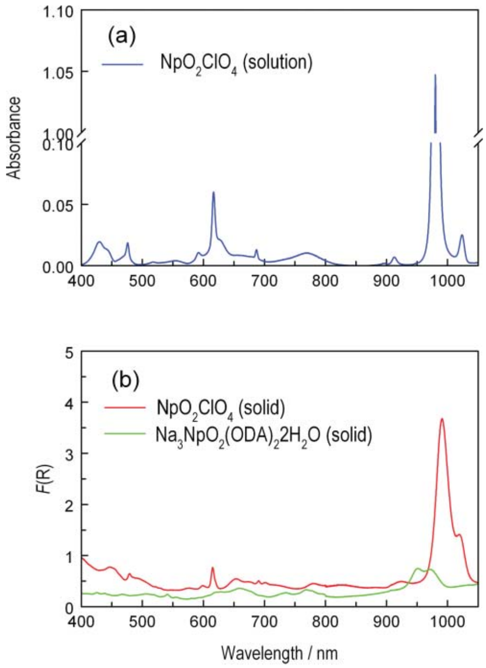


Fig. 4 Diffuse reflectance spectra of solid $Na_3NpO_2(ODA)_2{\cdot}2H_2O$ and $NpO_2ClO_4{\cdot}xH_2O$ (b), in comparison with the absorption spectra of NpO_2ClO_4 in solution (a).

The results of single-crystal X-ray diffractometry have shown that the 1 : 2 Np(V)–ODA complex forms and possesses an inversion center. These results have validated the interpretation of the absorption spectra of Np(V)–ODA systems by invoking the 1 : 1 and 1 : 2 complexes and assuming the 1 : 2 complex does not absorb.

The presence of an inversion center in the solid compounds of Np(V) molecules can also be proved by the absence of sharp bands that belong to the f–f transitions in the diffuse reflectance spectra. In this work, diffuse reflectance spectra of $Na_3NpO_2(ODA)_2{\cdot}2H_2O(s)$ and $NpO_2ClO_4{\cdot}xH_2O(s)$ were collected on a Cary-5G spectrophotometer with the diffuse reflectance accessory and are shown in Fig. 4, in comparison with the absorption spectra of free NpO_2^+ in solution. As Fig. 4 indicates, while the spectra of NpO_2^+ in solution and $NpO_2ClO_4{\cdot}xH_2O$ in solid show sharp peaks (980–989 and 620 nm) typical of f–f transitions, these peaks are absent in the diffuse reflectance spectra of $Na_3NpO_2(ODA)_2{\cdot}2H_2O$ solid because the f–f transitions are forbidden due to the symmetry of this compound. Again, these results are consistent with the theoretical calculations.[2]

In summary, the 1 : 2 Np(V)–oxydiacetate complex, $NpO_2(ODA)_2^{3-}$, was identified in solution by absorption spectroscopy and in the solid by single crystal X-ray diffractometry for the first time. The possession of an inversion center in this complex makes the f–f electric-dipole transitions of Np(V) forbidden, resulting in the "silence" of the absorption spectra of this complex in solution and the diffuse reflectance spectra of its solid compound in the near IR and visible regions. These results have validated the theoretical calculations of the probability of f–f transitions and, more significantly, have emphasized the importance of understanding the relationship between the spectroscopic features and symmetry and the necessity of using multiple spectroscopic techniques in characterization of actinide complexes. Failure to recognize the "silent" features of f–f transitions of centrosymmetric species in absorption spectra could result in the "missing" of such species and lead to incorrect speciation.

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12 *Crystal data*: $Na_3NpO_2(ODA)_2{\cdot}2H_2O$, $M_r = 674.18$, dimensions $0.07 \times 0.06 \times 0.05$ mm, triclinic, space group $P\bar{1}$, $a = 7.256(2)$, $b = 7.399(2)$, $c = 9.699(3)$ Å, $\alpha = 67.888$, $\beta = 87.284$, $\gamma = 67.771°$, $V = 8876\ (1)$ Å^3, $Z = 1$, $D_c = 2.523$ g cm^{-3}, $2\theta_{\max} = 58.46°$, $T = 223$ K, 3040 reflections collected, 1766 independent, $R_{int} = 0.0365$, absorption correction with SADABS,[13] refinement against $|F^2|$, $R_1 = 0.0302$ for 1766 collections ($wR2 = 0.0779$, $I > 2\sigma(I)$). A mild restraint was applied to all of the water O–H distances to ensure a reasonable and stable refinement. The small crystal was immersed in Paratone-N oil and sealed inside a quartz capillary (id = 0.2 mm). Precautions, including coating the capillary with a thin layer of protective resin, were taken to ensure the containment of radioactive neptunium. The capillary was mounted in a brass pin on the goniometer, which was then transported from the radiochemistry laboratory in a closed container to the ALS, thus minimizing the amount of alignment work required once at the diffractometer. Crystallographic data were collected in <1 h using a Bruker Platinum 200 detector at the ALS. CCDC 646382. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706825e.

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