The Raman Spectrum of $[U(NCS)_8]^{4-}$ and Configuration of the Ion in Solution

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Raman and i.r. spectra of $M_4[U(NCS)_8]$ (M = NEt_4 or Cs) have been measured on the solids and their solutions in nitromethane and acetonitrile in the ν_{CN} region. These data suggest that in these solvents the anion has an antiprismatic (D_{4d}) configuration.

It is known from *X*-ray studies on $[NEt_4]_4[U(NCS)_8]$ (**1**)[1] and on $Cs_4[U(NCS)_8]$ (**2**)[2] that in (**1**) the anion has the unusual cubic (O_h) configuration while in (**2**) it is Archimedean antiprismatic (D_{4d}); in both, the thiocyanate groups are bonded to the metal atom *via* their nitrogen atoms. There is dispute however in the literature as to the structure of the anion in solution. Infrared studies on (**1**)[3] and (**2**)[3,4] in nitromethane[3] or acetone[4] solutions suggest a D_{4d}[3,4] or a dodecahedral (D_{2d})[3] structure, but a very recent paper on the i.r. spectrum of (**1**) and of $[AsPh_4]_4[U(NCS)_8]$ in acetone solution suggests that the complex dissociates in this solvent, giving some free SCN^-, so that no structural data can be obtained from i.r. studies.[5] An i.r. and Raman study on (**1**) in the solid state and in solution suggested, however, on the basis of the observation of two Raman bands in $[^2H_3]$nitromethane, that the O_h symmetry of the solid is maintained in solution.[6] We have used Raman and i.r. spectroscopy in the ν_{CN} region, using both numbers and profiles of bands, to infer configurations of octacyano complexes in solution {*e.g.* $[Nb(CN)_8]^{4-}$ (ref. 7) and $[Nb(CN)_8]^{5-}$ (refs. 7 and 8)} and report here a similar approach for (**1**) and (**2**).

Results and Discussion

For $[U(NCS)_8]^{4-}$ with cubic (O_h) symmetry we expect two Raman-active ν_{CN} stretches ($A_{1g} + T_{2g}$; A_{1g} polarised) and one i.r. (T_{1u}) stretch; for the antiprismatic (D_{4d}) structure three Raman ($A_1 + E_2 + E_3$; A_1 polarised) and two i.r. ($B_2 + E_1$) stretches; and for dodecahedral (D_{2d}) symmetry six Raman ($2A_1 + 2B_2 + 2E$; A_1 polarised) and four i.r. ($2B_2 + 2E$) stretches. Only for the last will there be any Raman–i.r. coincidences (four). The Table shows that the spectra bear out these predictions for the solids. For (**1**), having O_h symmetry, there are indeed two Raman bands (the reported[6] extra shoulder at 2 040 cm^{-1} was not observed) while the i.r. spectrum shows one main band at 2 050 cm^{-1}, as earlier reported;[3] there are weaker bands at 2 130 and 2 110 cm^{-1} which may arise from solid-state effects. The spectrum of the antiprismatic[2] compound (**2**) has a quite different Raman profile of three bands as expected for D_{4d} symmetry, and there are two strong i.r. bands differing in frequencies from the Raman shifts. In solution in nitromethane or acetonitrile both (**1**) and (**2**) give the same spectra with *three* Raman bands, not two as previously[6] reported; there is an easily discernible depolarised shoulder near 2 055 cm^{-1} on the main depolarised band at 2 040 cm^{-1}, and there is one polarised mode as expected for the totally symmetric stretch. This spectrum clearly excludes the O_h structure which requires only two Raman bands and the dodecahedral structure which requires six, but is consistent with the antiprismatic (D_{4d}) structure. Furthermore the profiles of the Raman spectra of (**1**) and (**2**) in solution are very similar to the profile of the Raman spectrum of the antiprismatic solid (**2**). Although we used high-resolution conditions to study the i.r. spectra of the solutions we could observe, as did previous workers,[3,4] only one rather broad band at 2 048 cm^{-1}. That no free SCN^- from dissociation of the complexes was present in the solutions was shown by the absence of an i.r. or polarised Raman band at 2 057 cm^{-1} which is where solutions of $[PPh_4]SCN$ in nitromethane or acetonitrile absorb. These spectra have features in common with those of $[Nb(CN)_8]^{4-}$ (ref. 7) and $[Nb(CN)_8]^{5-}$ (refs. 7 and 8) in solution; for both of these Raman and i.r. data suggested a D_{4d} structure for the anions in solution with, as here, the polarised A_1 band lying highest in frequency with the i.r. band intermediate in frequency between the depolarised bands.

Table. Vibrational spectra[a] of $[U(NCS)_8]^{4-}$ salts

	$[NEt_4]_4[U(NCS)_8]$ (**1**)					$Cs_4[U(NCS)_8]$ (**2**)					Ref.
(*a*) Solid											
R		2 099(3)		2 047(10)		2 093(4)			2 050(4)	2 035(10)	*b*
		2 092(2)		2 047(10)	2 040 (sh)						6
I.r.	2 130w 2 110m		2 050vs			2 098w	2 086vs	2 064vs			*b*
			2 045s						2 050vs		3
(*b*) Solution											
R, CH_3NO_2		2 093(3)p	2 054(4)dp		2 042(4)dp	2 095(4)p			2 053(4)dp	2 037(10)dp	*b*
R, CH_3CN		2 093(4)p			2 052(10)dp						6
		2 095(4)p	2 057(3)dp		2 038(10)dp	2 095(4)p			2 057(3)dp	2 037(10)dp	*b*
I.r., CH_3NO_2					2 048vs			2 048vs			*b*
I.r., CH_3NO_2					2 060vs			2 045vs			3
I.r., $(CH_3)_2CO$							2 087m				4

[a] Values in cm^{-1}; R = Raman, p = polarised, dp = depolarised; relative Raman intensities in parentheses. [b] This work.

Experimental

The salts were prepared by methods similar to those used by Bagnall and co-workers.[3] For the tetraethylammonium salt, uranium tetrachloride (0.6 g, 1.58 mmol) was added to a mixture of potassium thiocyanate (1.23 g, 12.6 mmol) and tetraethylammonium chloride (1.05 g, 6.32 mmol) in dry acetonitrile (10 cm^3) under argon. The mixture was stirred gently for 15 min and filtered to remove precipitated potassium chloride. The light green filtrate was cooled to -20 °C to yield green crystals. For the caesium salt, uranium tetrachloride (1.12 g, 2.95 mmol) was added to a solution of caesium chloride (4.5 g, 20 mmol) in acetone (20 cm^3) and the solution warmed with stirring under argon; the hot solution was filtered to remove caesium chloride and the filtrate cooled. The acetone was removed on a vacuum line and the residue taken up in nitromethane (10 cm^3), filtered and dichloromethane (20 cm^3) added. Cooling overnight produced green crystals of the product (Found: C, 7.5; N, 7.1; S, 19.9. $C_8Cs_4N_8S_8U$ requires C, 7.8; N, 9.1; S, 20.8%).

Raman spectra were measured on a Spex Ramalog 5 spectrometer on supported spinning KBr discs or on solutions in sealed capillaries under argon using a krypton model 52 CRL laser with excitation at 5 682 and 5 308 Å; i.r. spectra were measured on Perkin-Elmer 683 and 983G instruments in Nujol mulls and, as solutions, in NaCl cells.

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