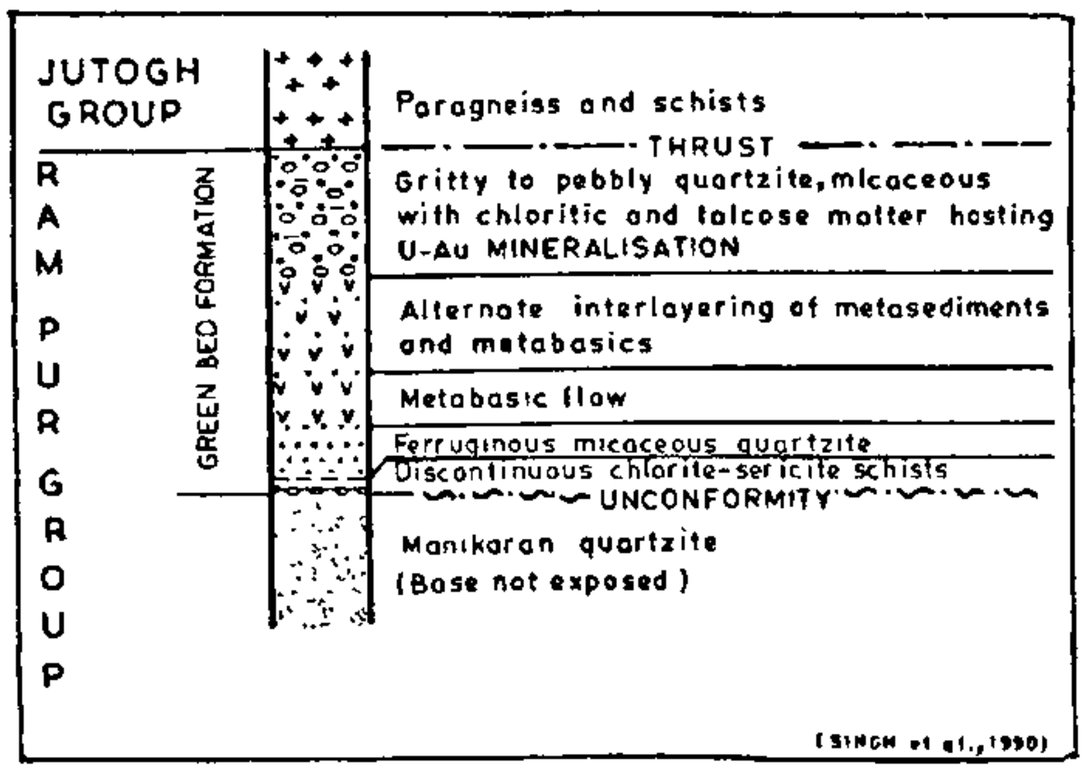

Figure 2. Lithotectonic sequence showing the position of U–Au mineralization in Nogli Valley.

schists of the Jutogh Group[2]. The lithotectonic sequence indicating the position of the U–Au occurrence is shown in Figure 2.

Uranium and gold mineralization follow a NE–SW-trending shear zone dipping gently due SE and traceable intermittently for 650 m along a subvertical scarp. The host rock is a mylonite consisting of quartz, sericite and chlorite, with minor amount of biotite. Tourmaline, zircon, ilmenite, rutile, uraninite and black opaques occur as accessories. Sulphide minerals are conspicuously absent. The quartz grains indicate both metamorphic and igneous provenance, and are of two different sizes. The larger grains are occasionally pebbly in size, generally flattened, and aligned along the foliation, but at times also occur oblique to it. The flaky minerals veer around the larger quartz grains. Uranium minerals identified are uraninite and autunite. No discrete gold, however, could be observed under the petrological microscope.

Gold was determined by flameless atomic absorption spectrometry. The sample was decomposed with hydrofluoric acid, aqua regia and hydrobromic acid–bromine solution. Gold was extracted in methylisobutylketone from sample solution adjusted to 0.1 M hydrobromic acid. Final determination of gold was done using a Varian AA-475 atomic absorption spectrometer equipped with a Varian CRA-90 carbon rod atomizer. Uranium was determined by routine radiometric method.

Uranium and gold values have wide dispersion. The range, mean and standard deviation for 25 samples from this area are as follows:

	Range	Mean	Standard deviation
U_3O_8 (wt %)	<0.01 to 1.0	0.217	0.381
Au (ppm)	0.03 to 20.00	0.32	0.768

The sample analysing 20 ppm gold has not been included in the calculations for mean and standard deviation.

Studies are in progress to evaluate the economic viability of this occurrence as well as paragenetic relationship of uranium and gold. The uranium–gold association enhances the resource potential of this area and opens up the possibility of locating gold mineralization in other parts of the Rampur Window and Himalaya under similar lithostructural settings. Airborne radiometric surveys could help in quick identification of such occurrences.

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Fluorescence characteristics of 1,3-, 1,4-, 2,3- and 2,7-dihydroxynaphthalene radical cations

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We have recorded excitation and fluorescence spectra of 1,3-, 1,4-, 2,3- and 2,7-dihydroxynaphthalene radical cations in a rigid matrix. While the parent compounds give rise to broad and structureless emission bands, the ionic spectra exhibit, in addition to an intense band, a few weaker bands. Excitation wavelength and fluorescence maxima for the cations are shifted towards longer wavelength compared to those for the parent molecules. The characteristic features of the spectra are explained in relation to the position of –OH groups in the molecule.

MANY naphthalene derivatives are fluorescent, a property attributed to π-electron excitation. A substituent group such as –OH has unshared electron pairs that can be transferred into vacant π orbitals belonging to the aromatic ring. This effectively raises the ground-state energy of the π-electron system. Thus the absorption and fluorescence of the -OH-substituted molecule occur at lower frequencies. When two donor groups are attached to the aromatic ring, the positions of absorption and fluorescence bands are usually

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determined by the more strongly interacting group. Absorption and fluorescence spectra of mono- and dihydroxynaphthalene isomers have been available for a long time[1–7]. Absorption data for both 1- and 2-naphthol cations have been reported recently[8]. However, dihydroxynaphthalene radical cations have received little attention and no published data on their absorption and fluorescence are readily available. In this paper, we report the fluorescence characteristics of radical cations of some dihydroxyl substituted naphthalenes. The compounds selected for the present investigation are: 1,3-, 1,4-, 2,3- and 2,7-dihydroxynaphthalenes (DHNs). Their radical cations have been obtained by photo-oxidation of their rigid solutions in boric acid glass.

The DHNs (Fluka) were used without further purification. Boric acid crystals (IDP, Hyderabad) were heated to about 240 C in an oven and a small quantity of the hydrocarbon under consideration was added to it. After thorough mixing, the resultant mixture was sandwiched between two glass plates which formed a transparent rigid glass after cooling to room temperature. The hydrocarbon-doped boric acid films were irradiated with an Osram 125 W high-pressure mercury lamp The excitation and fluorescence emission spectra were recorded using an Aminco–Bowman spectrophotofluorometer at room temperature (~25°C). These spectra have been corrected for the nonlinear response of the detector photomultiplier tube (IP-21) and the nonuniform emission of the excitation source, the xenon lamp.

The values of λ_{ex} and λ_f for the DHN molecules and their radical cations are listed in Table 1. λ_{ex} represents the longest excitation wavelength in the visible region for which the intensity of fluorescence emission is maximum. In the column λ_f for the radical cations, in addition to the most intense fluorescence band, other weaker bands are also listed.

The fluorescence spectra of the radical cations in boric acid glass are shown in Figure 1. The spectrum of the ionic species is characteristic of the position at which ionization occurs and the orientation of the substituent group. An –OH group has unshared electron pairs, which get transferred into vacant π orbitals belonging to the aromatic ring. Thus the π electrons from the aromatic system are delocalized and get transferred onto the functional group. This process is further enhanced on ionization and causes a bathochromic shift of the absorption and fluorescence maxima. Table 1 indicates that λ_{ex} ($\approx \lambda_{ab}$) and λ_f for the cations are shifted towards longer wavelength compared to those for the parent molecules. It is also observed that, while the fluorescence spectra of all the compounds in the molecular form give rise to only one broad and structureless electronic band, their ionic spectra exhibit, in addition to an intense band, a few weaker bands. These weaker bands probably arise owing to the vibrational structures associated with these species. The most intense band at 475 nm of 1,4-DHN has vibronic bands on either side at 452, 464 and 500 nm. There is a good agreement between the frequencies of these bands and the frequencies of vibrational bands reported in the literature[9]. Van Gemert[9] has reported that all the DHNs in which one or both of the OH groups are in α position possess a medium-intensity vibrational band at 1040 cm^{-1}. In the present case of 1,4-DHN, the band at 500 nm on the lower-energy side is shifted by 1050 cm^{-1} from the main band and those on the higher-energy side are shifted by 500 and 740 cm^{-1}, which are of the right magnitude to be due to vibrational relaxation. Similarly, the vibronic bands in other cationic fluore-

Table 1. Excitation and fluorescence emission maxima (nm) of dihydroxynaphthalenes in boric acid glass

	Parent molecule		Radical cation	
Compound	λ_{ex} (nm)	λ_f (nm)	λ_{ex} (nm)	λ_f (nm)
1,3-DHN	331	381	387	410 (w) 458 (m) 490 (s)
1,4-DHN	327	390	378	452 (sh) 464 (sh) 475 (s) 500 (m)
2,3-DHN	322	346	398	426 (sh) 452 (s) 480 (sh) 490 (sh)
2,7-DHN	323	342	379	420 (sh) 450 (sh) 474 (s) 507 (m)

w, weak, m, medium, s, strong, sh, shoulder.

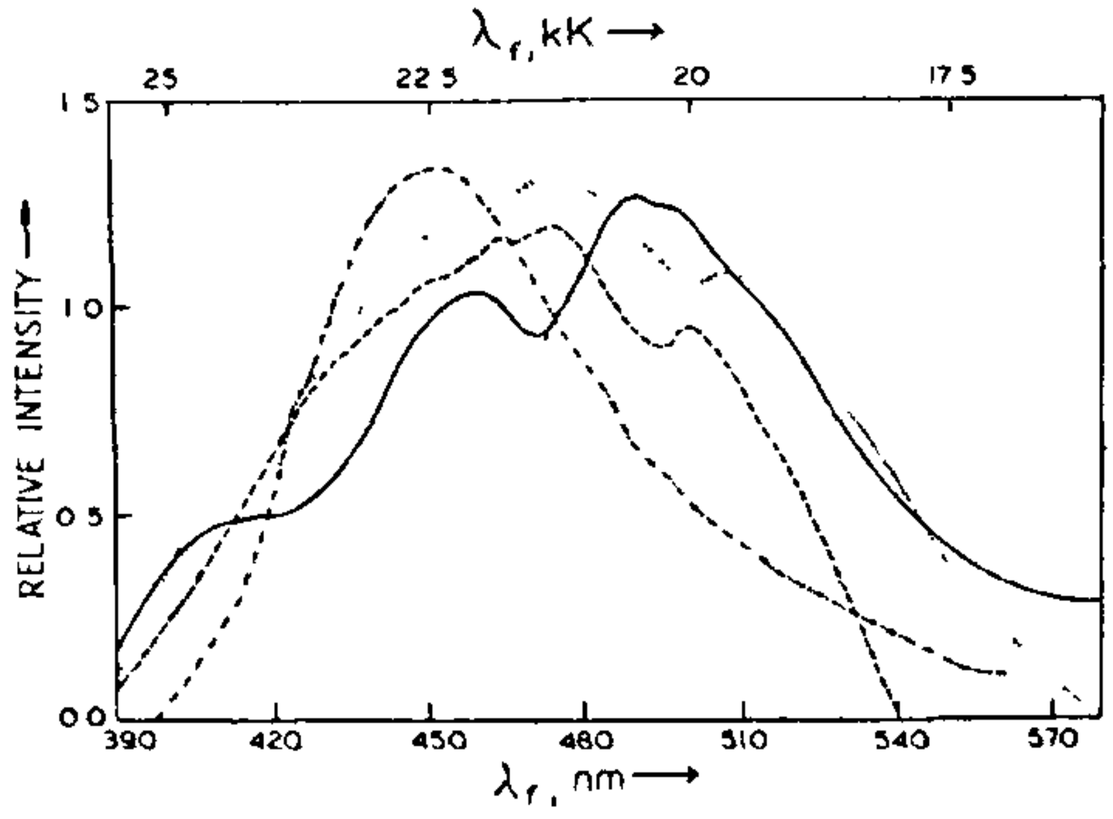

Figure 1. Fluorescence spectra of dihydroxynaphthalene radical cations (conc. ~0 005 wt%) in boric acid glass: ———, 1,3-DHN, – –, 1,4-DHN, –·–·–, 2,3-DHN, ..., 2,7-DHN.

scence can be identified. The fact that the vibronic bands are more pronounced in the cationic fluorescence indicates larger reorientation of the ionized substituent group in the excited-state configuration, involving nuclear motion and hence dissipation of energy. However, in the ionic fluorescence spectrum of 1,3-DHN a weak band is found at 410 nm, which probably arises from a separate electronic transition rather than owing to vibrational fine structure. Furthermore, it can be seen that the fluorescence of the cations shows a larger red shift compared to the absorption. This indicates a greater degree of interaction between the ionic substituent group and the aromatic ring in the excited state than in the ground state. In such a case, the energy of vibrational relaxation in the excited state will be greater than that in the ground state. Consequently, the shifting effect of the ionic substituent upon the fluorescence spectrum will be greater than its shifting effect upon the absorption spectrum relative to the spectrum of the parent molecule. In the case of 2,3-DHN and 2,7-DHN one expects intense fluorescence due to strong horizontal polarization of two substituted groups. It is worth noting that the major ionic emission maximum of 2,7-DHN is more redshifted in comparison to that of 2,3-DHN. This difference could be due to the proximity of –OH groups at positions 2 and 3, which could give rise to intramolecular hydrogen bonding.

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Crystal structure of hexanediamine–glutamic acid complex

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Polyamines are some of the most important and ubiquitous small molecules that modulate several functions of plant, animal and bacterial cells. Despite the simplicity of their chemical structure, their specific interactions with other biomolecules cannot be explained solely on the basis of their electrostatic properties. To evolve a structural understanding on the specificity of these interactions it is necessary to determine the structure of complexes of polyamines with other, representative biomolecules. This paper reports the structure of the 1:2 complex of hexanediamine and L-glutamic acid. The complex crystallizes in the monoclinic space group $P2_1$ with $a=5.171(1)$ Å, $b=22.044(2)$ Å, $c=10.481(2)$ Å and $\beta=104.51(1)°$. The structure was refined to an R factor of 6.6%. The structures of these complexes not only suggest the importance of hydrogen-bonding interactions of polyamines but also provide some insight into other complementary interactions probably important for the specificity of biomolecular interactions.

POLYAMINES modulate a variety of cellular functions in plants, animals and bacteria[1]. They are integral components of tRNA and other anionic molecules. They also appear to interact with membrane components in several plant tissues, and such interactions result in modified permeability and delayed senescence of extracted leaves[2]. Considering the simplicity of the chemical structure of polyamines, it is surprising that a clear understanding of their interactions does not exist. Part of the reason is the nonavailability of the molecular structures of the complexes of these amines with other ubiquitous biomolecules. To provide information on these interactions, we have earlier determined and reported structures of complexes of putrescine with glutamic acid[3] and aspartic acid[4]. In this paper we report the structure of hexanediamine–glutamic acid complex, and discuss the nature of the interactions of the longer amine hexanediamine with glutamic acid in the context of the structures reported earlier.

Crystals of 2:1 complex of L-glutamic acid and hexanediamine were obtained by slow diffusion of propanol into an aqueous solution of the complex. On X-ray examination, the crystals were found to be monoclinic $P2_1$ with $a=5.171(1)$ Å, $b=22.044(2)$ Å, $c=10.181(2)$ Å, and $\beta=104.51(1)°$. Two glutamic acid and one hexanediamine molecules, when assumed to be present in the crystal asymmetric unit, give a calculated density of 1.21 g cm^{-3}. This value is less than the density of the crystals of complexes of glutamic and aspartic acid with putrescine.

X-ray diffraction intensities were recorded to 0.84-Å resolution using an Enraf–Nonius 4-circle diffractometer by $w/2\theta$ scan. The X-ray source was a microfocus sealed tube with a molybdenum anode ($\lambda=0.7107$ Å). Reflections with $k\geqslant 0$, $l\geqslant 0$ were recorded, resulting in a total of 2028 unique measurements. The reflection intensities were corrected for Lorentz and polarization factors.

The structure was solved by direct methods using the program MULTAN[5]. After initial refinement of C, N and O atoms of the complex, using a block-diagonal structure factor least-squares program originally written