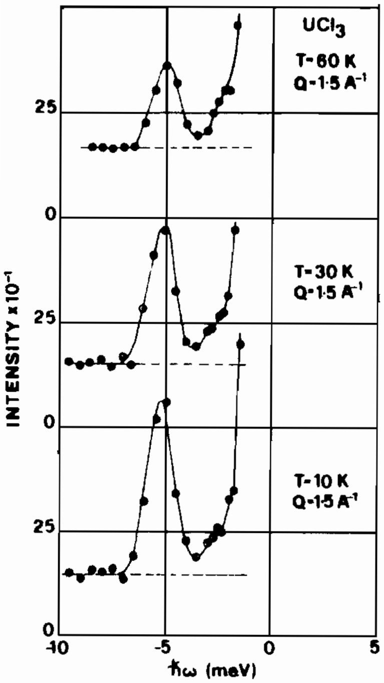

Fig. 1. Energy spectra of neutrons scattered from 1D antiferromagnet UCl_3 at various temperatures. The curve is drawn as a guide to the eye.

In spite of the fact that both substances appear to be a good example of 1D system, the hypothesis of the existence of linear antiferromagnetic chains in UBr_3 and UCl_3 needs direct experimental confirmation. Of course, for powdered sample the diffraction method is useless but the neutron spectroscopy can provide some valuable informations even if they are masked due to polycrystalline nature of the sample.

The measurements to be presented here were performed on a triple axis spectrometer at Wurenlingen working in the constant Q mode and scanning the incident neutron energy. The outgoing energy was fixed at 15 meV. Various energy loss configurations at different temperatures and with different incoming neutron energies were realized to cover energy transfers ħω up to 65 meV. To a first sight all observed lines of magnetic origin might be attributed to crystal-field transitions from the ground state to the excited states since the intensities of ground state transitions decrease with increasing temperature. On the other hand, recently published optical crystal spectra for U_3: in $LaCl_3$ preclude up to ~25 meV any CF excitation from the ground state [4]. Therefore the inelastic scattering of neutrons corresponding to energy transfers of ~5 meV and ~4 meV in UCl_3 and UBr_3 respectively, appears to have now a very simple explanation: most likely it corresponds to the excitation of 1D system. Such excitations are quasi 1D spin waves which propagate along individual chains.

Theory predicts that for the momentum components perpendicular to the chains these excitations are dispersionless, whereas along the chain direction, dispersion relation should follow a perfect sine curve. In powder measurements possible dispersion effects are most likely smeared out due to the polycrystalline nature of the sample. From Fig. 1 it is seen that as the temperature is raised, the 5 meV excitation in UCl_3 decreases rapidly, but there is no appreciable change either in peak position or in its linewidth. The same feature was noticed in earlier measurements on UBr_3 where damping of the 4 meV excitation was even more severe, but also no apparent change in its halfwidth was detected even at 100 K. This result is not quite surprising as might first appear, since as a consequence of the low dimensionality, the length over which the spins are correlated will be larger than in 3D systems at the same temperature relative to T_N or T_c. As a result, in Ising systems well defined excitations were detected at temperatures as high as 10 T_N [5].

The spin wave linewidth in 1D system is mainly due to the finite correlation length and the excitations which are very sharp for $T < T_N$ and usually limited only by the instrumental resolution, broaden rapidly with increasing temperature. This fact is in sharp contrast with our measurements and represents a major puzzle that is not understood. Clearly more systematic study, possibly on the single crystals would be most welcome.

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The Quantum Chemical Interpretation for the Cation–Cation Interactions

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The pentavalent actinides AnO_2^+ where An = U, Np, Pu, and Am show the interaction with some active cations like UO_2^{2+}, Fe^{3+}, Th^{4+}, In^{3+} etc. [1–5].

In the present work the mechanism for the cation–cation interactions (CCI) is proposed and the quantum chemical explanation is given for the experimental regularities. The orbital symmetry theory is extremely useful in understanding CCI. In this theory [6] the interaction between two systems, *e.g.* the uranyl(VI) and the AnO_2^+ is due to the overlapping between the occupied and empty molecular orbitals (m.o.) with the appropriate symmetry. These are the occupied σ_u and the empty or partially occupied δ_u m.o. On the theoretical side, the calculations show that the energies E for σ_u^2 and δ_u levels in the UO_2^{2+} are equal to –25.77 and –22.78 ev respectively whereas in the UO_2^+ they are equal to –17.75 ev and –14.06 ev. In this energy relation the CCI by its nature is a donor–acceptor type. The energy gap between the occupied and empty m.o. Δ in the cations is of crucial importance in their interaction. When $\Delta > 0$, the σ_u occupied m.o. in the UO_2^+ donates an electron density to the empty δ_u m.o. in the UO_2^{2+}. The symmetry of the transition state in the UO_2^{2+}—AnO_2^+ interaction results in the $U^{VI}\cdots O—U^{V}—O$ bond formation. When Δ takes on a negative value *i.e.* the acceptor level is above the donor one the CCI cannot occur. This approach explains why the plutonyl ion shows no interaction with the uranyl(VI) ion. The donor level in the PuO_2^{2+} ion has a lower energy than this level in the UO_2^{2+}. In other words the PuO_2^{2+}———UO_2^{2+} CCI is less probable than the UO_2^{2+}———UO_2^{2+} CCI. The main cause is a negative value of Δ. The levels which are occupied by extra electrons are left non-bonding for CCI. The main difference in the NpO_2^+ and PuO_2^{2+} is the position of the donor σ_u m.o. relative to the acceptor m.o. in the UO_2^{2+}. In the AnO_2^+ ions the last bonding m.o. are progressively more stable when the An atomic number increases. This means that the σ_u m.o. in AnO_2^+ is brought closer together with the acceptor δ_u m.o. in the UO_2^{2+}. The energy gap value reduces and the CCI strength weakens.

With the partially occupied acceptor level its ability to draw an electron density from the donor level weakens owing to electron–electron repulsion. As the number of electrons on the non-bonding acceptor level increases, NpO_2^{2+}, PuO_2^{2+}, and AmO_2^{2+} the CCI with the AnO_2^+ weakens; the acceptor level occupancy has the effect on the CCI strength in addition to the energy gap value.

The electron density distribution in the AnO_2^{2+} ions can form the basis of the explanation for the CCI since the oxygen effective charges may be related directly to the position of the σ_u donor level. So the large netative oxygen charge in the AnO_2^+ corresponds to the rise of the σ_u level, an increase of the energy gap and the strengthening CCI. So in the pentavalent ions the effective charges are

–0.915 +2.83 –0.915
O———U———O

and

–0.8 +2.6 –0.8
O———Am———O

As one would expect the m.o. and the 'chemical' opinions about the CCI are in line. But the idea of the effective charges is often inadequate to explain the CCI. *E.g.* there is excess negative charge on the oxygen atoms in the UO_2^{2+} in comparison with the AmO_2^{2+}. However the CCI between these ions when the uranyl(VI) ion is the ligand to the americyl(VI) ion is not observed.

The complexation capacity of the active cations increases with a decreasing energy ν corresponding to a charge transfer band in water complexes of these cations [5]. There is the order $\nu_{UO_2^{2+}} < \nu_{Fe^{3+}} < \nu_{Th^{4+}} < \nu_{In^{3+}}$ but the complexation ability changes in the contrary direction. The value ν in the water complexes is determined as $\nu = E_L - E^*$ where E_L is the energy of the oxygen 2p orbitals in the H_2O and E^* is the energy of the acceptor of the metal or actinide ion orbital. The charge transfer band energy is determined by the E^* value. On the other hand the CCI strength depends on the value of the energy E^* acceptor level too.

The experiment shows both the ν_1 symmetric band shift, $\Delta\nu_1 > 0$ and $\Delta\nu_1 < 0$ in the vibrational modes of the NpO_2^+ in the cation complexes of this ion, *e.g.* with the UO_2^{2+} and the Cu^{2+} in the $Cu(H_2O)_6^{2+}$ four molecules in the equatorial plane being more strongly held than the two more distant axial molecules owing to the Yahn–Teller effect. In the $UO_2(H_2O)_4^{2+}$ four water molecules in the equatorial plane are more distant than two oxygen axial atoms *i.e.* in aqua solution the cupric ion is elongated but the uranyl ion is compressed. In the former the axial H_2O but in the latter ion the equatorial H_2O molecules can be replaced by the oxygen atom in the NpO_2^+. So in the cation–cation complex . . .Cu———O_I—Np———O_2 the distance Np–O_I is shorter than the Np–O_2 but in the . . .U—O_I———Np—O_2 the opposite is true. The theoretical explanation in molecular orbital terms for the shift of the main peak towards the red end in the AnO_2^+ ions was made by us. Finally we think that of partial significance to CCI understanding is the fact that the mixed valent crystals can bridge the data obtained on solution samples since PtF_3 which is $Pt^{II}Pt^{IV}F_6$, $Cs_2Ag^{I}Au^{III}Cl_6$ simulate the 'cation–cation' crystal [8].

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B15

Spectroscopy of Holmium Glasses

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The electronic energy levels of holmium in fluoride glasses of the composition $57ZrF_4 \cdot 36BaF_2 \cdot 3LaF_3 \cdot 4AlF_3 \cdot 4AlF_3$ were calculated by the diagonalization of the energy matrices of the $4f^{10}$ configuration including electrostatic and spin–orbit interactions as well as the α (Trees) β and γ (Casimir operator) corrections.

The observed spectra of holmium in these glasses were fitted by least-squares calculations to the 7 radial parameters involved to obtain the latter's best values.

The resulting intermediate coupling eigenvectors were used for the calculation of the squares of the reduced matrix elements between any pair of energy levels, thus giving the spectroscopic characteristics of the transitions in the energy range between 5000 and 25000 cm^{-1}.

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Photophysical and Photochemical Properties of Europium Cryptates

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Several diazapolyoxabicyclic ligands ('cryptands') [1, 2] are able to encapsulate metal ions to form coordination compounds ('cryptates') which have been the object of extensive thermodynamic, kinetic, structural, electrochemical, and analytical investigations [2–12]. By contrast, only a few studies [12–14] have been reported on the electronic absorption and emission spectra of these compounds because both the cryptands and, in most cases, the encapsulated metal ions are spectroscopically 'mute' species. The spectroscopic behavior of rare earth complexes is a topic of great interest, both theoretical [15–17] and applicative [18–20]. We have thus begun spectroscopic studies on cryptates containing europium or other rare earth ions.

The spectroscopic and photophysical properties of the complexes between En^{2+} and the 2.2.1 and 2.2.2 cryptands are reported and compared to those of the Eu^{2+} aquo ion. Both complexes show broad, relatively intense absorption bands in the near u.v. region due to $4f^7 \rightarrow 4f^6 5d$ transitions. Some weak narrow bands due to transitions within the $4f^7$ configuration also appear in the 310–320 nm region. Both complexes exhibit a strong blue luminescence from $4f^6$. At 77 K the emission quantum yield is unity, and some vibrational structure can be observed in the broad emission band. Luminescence is also maintained in aqueous solution at room temperature with τ of the order of a few nanoseconds, and ϕ of the order of 10^{-3}, in contrast with the behavior of the Eu^{2+}_{aq} ion which does not exhibit any luminescence emission under such conditions. The results obtained are discussed in the light of the interaction between Eu^{2+} and water molecules and of the size and symmetry of the cryptand cage.

The spectroscopic and photophysical properties of the Eu^{3+} complex of the 2.2.1 cryptand are investigated in aqueous solution. The absorption spectrum of the complex, besides the f → f transition of the Eu^{3+} ion, shows two broad bands at 298 and 248 nm (ϵ, 111 and 93, respectively) which are assigned as charge transfer transitions from N and, respectively, O atoms of the ligands to Eu^{3+}. High resolution emission spectra show that in aqueous solution there is only one Eu-containing species with C_{2v} symmetry. The emission quantum yield is 3×10^{-2} upon excitation at 393 nm in the $^5L_6$ metal centered band and 3×10^{-3} and 1×10^{-3} upon excitation in the charge transfer bands at 350 nm and 260 nm, showing that the conversion of the charge transfer levels to the $^5D_0$ emitting state is relatively inefficient. Luminescence decay measurements in H_2O and D_2O solutions and comparison with the data obtained for Eu^{3+}_{aq} show that encapsulation of Eu^{3+} in the cryptand cage does not shield the metal ion towards interaction with solvent since three water molecules are still coordinated to Eu^{3+} through the cryptand holes.

The emission of [Eu^{3+} C 2.2.1] is quenched by $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Mo(CN)_8^{4-}$ with $K_q = 6.4 \times 10^8$, 1.9×10^8, 1.2×10^9 l mol^{-1} sec^{-1}, respectively. The quenching takes place via charge-transfer interaction, as shown by the appearance of a new