Table I. Spectral and Thermodynamic Data for the $[\mathrm{Eu}\subset 2.2.1]^{3+}$–$M(CN)_6^{4-}$ Ion Pairs[a]

$M(CN)_6^{4-}$, $E_{1/2}^{b}$, V	λ_{max}, nm	ϵ_{max}, $M^{-1}\,cm^{-1}$	$\Delta\nu_{1/2}$, cm^{-1}	K_{IP},[c] M^{-1}
$Fe(CN)_6^{4-}$, +0.19	530	110	6100	300[d]
$Os(CN)_6^{4-}$, +0.40	450	110	7800	800
$Ru(CN)_6^{4-}$, +0.70	434	120	6500	400

[a] Aqueous solutions, KCl 1 M, 295 K. [b] Reference 5e. [c] From spectrophotometric titrations; uncertainty, ±10%. [d] 250 ± 50 M^{-1} from electrochemical measurements.

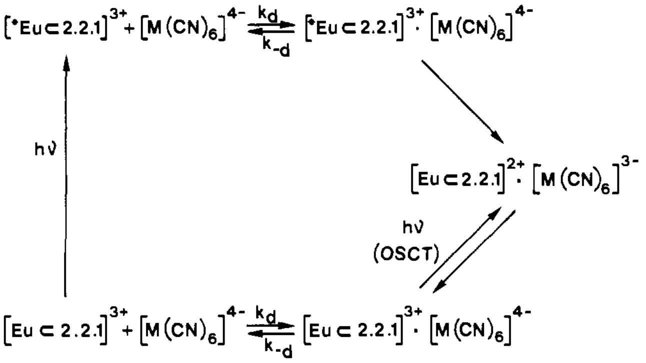

Figure 1. Scheme of the light-induced and thermal reactions occurring in the $[\mathrm{Eu}\subset 2.2.1]^{3+}$–$M(CN)_6^{4-}$ systems (M = Fe, Ru, or Os).

solution to 3 mL of a 5.0×10^{-3} M $[\mathrm{Eu}\subset 2.2.1]^{3+}$ solution caused the appearance of a violet color owing to the formation of a broad band with maximum at 530 nm. $Ru(CN)_6^{4-}$ and $Os(CN)_6^{4-}$ exhibited a similar behavior, giving rise to bands with maxima at 434 and 450 nm. The displacement of the absorption maximum toward the UV region as the cyanide complex becomes more difficult to oxidize (Table I) suggests that the new band is due to CT transitions within $[\mathrm{Eu}\subset 2.2.1]^{3+}$–$M(CN)_6^{4-}$ ion pairs. Spectrophotometric and potentiometric titrations in 1 M KCl showed that the ion pairs have a 1:1 stoichiometry[13] and allowed us to obtain the values of the formation constants which are reported in Table I together with the parameters of the observed OSCT bands. It should be noted that such bands are very broad and asymmetric, as expected because of their composite nature due to the splitting of the d^5 core of the oxidized hexacyano ion caused by spin–orbit coupling.[5e,14] The Gaussian analysis of the observed bands and a discussion of the kinetic parameters that can be obtained from the spectroscopic data[4b,5e,6a,c] will be reported in a later publication. As far as the formation of ion pairs and the appearance of OSCT transitions are concerned, our systems are quite similar to the Ru^{III} (amine)–$M(CN)_6^{4-}$ systems recently described by Curtis and Meyer.[5e] A noticeable difference is that the ion pairs described in this paper are quite stable both in the dark and under light excitation, while Curtis and Meyer's ion pairs are not stable, giving rise to cyano-bridged species in a few minutes.

Figure 1 summarizes the dark and light-induced reactions taking place between $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $M(CN)_6^{4-}$ and shows some important features of these systems where both ETQ and OSCT transitions can be observed. In sufficiently concentrated solutions the two complexes give rise to ground-state ion pairs. OSCT transitions can then occur, which lead to ion-pair species where the europium ion is reduced and the metal of the cyanide complex is oxidized. Since no net chemical effect is observed upon excitation in the OSCT band, the photoinduced OSCT reaction must be followed by a fast back-electron-transfer process which leads the system in its original situation. In diluted solutions ion pairs are not present, and light excitation of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ (e.g., at 394 nm) leads to the long-lived $^5D_0$ excited state of the europium complex, which is dynamically quenched by $M(CN)_6^{4-}$ via formation of an encounter (precursor) complex.[15] Such a reductive quenching leads to a successor complex which is exactly the same species as that obtained upon OSCT excitation of the ground-state ion pair. It is interesting to note that the thermal and the two light-induced electron-transfer reactions (Figure 1) are expected to exhibit the same intrinsic barrier and orbital overlap because the $^5D_0$ excited state of the europium complex has the same equilibrium geometry and the same orbital configuration as the $^7F_0$ ground state. These reactions, however, are not expected to behave in the same way as far as spin is concerned. The possible spin values are in fact 3 for the ground-state ion pair, 3 and 4 for the successor complex, and 2 for the precursor complex. Thus, the reductive quenching process is spin forbidden while the other two reactions are spin allowed. A very large influence of the spin factor, however, cannot be expected in these systems because of the presence of heavy atoms.

Further investigations on systems showing OSCT transitions and ETQ are needed in order to elucidate the role of the nuclear, orbital, and spin factors in these electron-transfer processes.

Acknowledgments. We thank Prof. M. Mastragostino for advice in measuring the ion-pair formation constant by means of electrochemical measurements. Financial support from the Ministero della Pubblica Istruzione e Consiglio Nazionale delle Ricerche is gratefully acknowledged.

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(13) Under suitable conditions evidence for formation of 2:1 species $\{[\mathrm{Eu}\subset 2.2.1]^{3+}\}_2$–$M(CN)_6^{4-}$ was also obtained.

(14) Griffith, J. S. "The Theory of Transition-Metal Ions"; University Press: Cambridge, 1961.

(15) In principle, the same precursor complex could be obtained via excitation of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ moiety of the ground-state ion pair. In practice, however, this is difficult because the weak absorption bands of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ are hidden by the broad and intense OSCT band.

Imidazole–Trimethyl Phosphate System: Characterization of the Hydrogen Bonding by Fast-Atom-Bombardment Mass Spectrometry and X-ray Crystallography

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The hydrogen-bonding properties of imidazole and its derivatives are of considerable importance in biochemistry. Of special interest is the ability of imidazole to form strong, easily polarizable hydrogen bonds as this may play an important role in a number of biochemical functions including proton conductivity in membranes[1] and protein oxygen binding.[2] An apparently simple example of a strong, easily polarizable hydrogen bond to imidazole has recently been reported to occur in the imidazole–trimethyl phosphate system.[3,4] Infrared and multinuclear NMR spectroscopy revealed the presence of the hydrogen bond and several other features of interest in the system but gave little information on the structure

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(1) Zundel, G. In "The Hydrogen Bond, Recent Developments in Theory and Experiments"; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Chapter 15.

(2) For recent examples see: Shaanan, B. *Nature (London)* **1982**, *296*, 683. Phillips, S.E.V.; Schoenhorn, B. P. *Ibid.* **1981**, *292*, 81. Quinn, R.; Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 2588. La Mar, G. N.; De Ropp, J. S.; Chacko, V. P.; Satterlee, J. D.; Erman, J. E. *Biochim. Biophys. Acta* **1982**, *708*, 317 and references therein.

(3) Clark, J. H.; Green, M.; Madden, R. G. *J. Chem. Soc., Chem. Commun.* **1983**, 136.

(4) For general discussions on strong hydrogen bonding, see: Emsley, J. *Chem. Soc. Rev.* **1980**, 91. And Chapter 12 in ref 1.

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Table I. Positive Ion FAB MS of the Complex in Glycerol[a]

m/z	rel intensity	assignment[b]	m/z	rel intensity	assignment[b]
69	100	$(I + H)^+$	195	17.60	$(IP + H)^+$
109	1.01	$(P - OH)^+$	263	2.40	$(IP + I + H)^+$
127	6.24	$(P + H)^+$	321	2.43	$(IP + P + H)$
137	3.21	$(I_2 + H)^+$	390	0.55	$(IP + H_2)^+$

[a] The sample was inserted on a stainless steel probe tip into the mass spectrometer (a kratos MS-30 with a DS-55 data system) and sputtered into the gas phase as ions by bombardment with 6 keV neutral xenon atoms. [b] I = imidazole; P = $(MeO)_2PO_2H$; IP = complex.

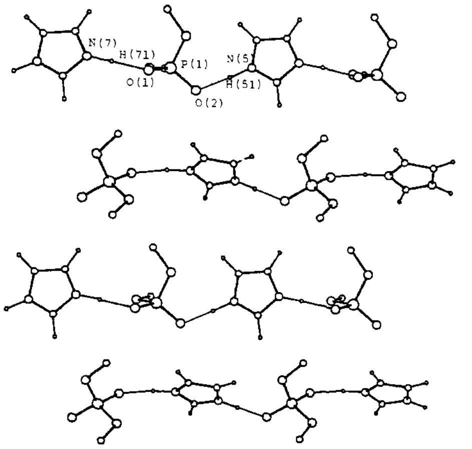

Figure 1. Diagram of the packing and chain-type structure of the imidazole-$(MeO)_2PO_2H$ complex. The positions of the hydrogen atoms have been geometrically calculated.

of the complex formed. We now wish to report the first use of fast-atom-bombardment mass spectrometry (FAB MS) as a means of characterizing a complex containing a strong hydrogen bond. The structure of the complex has been independently confirmed by conventional X-ray crystallography.

Ordinary electron-impact mass spectrometry (EI MS) of the crystals isolated from an equimolar mixture of imidazole and trimethyl phosphate gave the highest mass peak at m/z 126 followed by peaks characteristic of the fragmentation of imidazole and the phosphate. Such an experiment requires thermal volatilization of the complex and subjects it to bombardment with electrons, the combination of which effectively precludes the use of EI MS for the analysis of hydrogen bonding. In an attempt to overcome this problem we have used FAB MS, which as a soft ionization technique that does not require sample heating may allow the direct observation of hydrogen-bonded species.

The FAB MS of the crystalline complex dissolved in glycerol shows the three most intense peaks occurring at m/z 69, 127, and 195. Significant higher mass peaks at m/z 263, 321, and 390 were also observed in a remarkably clear spectrum. It is interesting to note that the complex is obviously strong enough to survive the hydrogen-bonding competition provided by the hydroxylic solvent and that it does not significantly dissociate in solution as this would be expected to produce intense fragments containing glycerol. We believe that the observed spectrum is only consistent with a polymeric complex of imidazole with $(MeO)_2PO_2H$ (Table I).

In order to disprove the possibility that the observed imidazole-phosphate species were produced by reactions between fragment species in the desorption-ionization process, systems containing imidazole and weaker hydrogen-bond electron donors were investigated. The FAB MS of imidazole-Ph_2O, imidazole-Ph_2CO, and imidazole-dioxane systems in glycerol gave spectra very similar to that of imidazole itself with no evidence of any peaks due to the hydrogen-bonded complexes. The more powerful hydrogen-bond electron donor Ph_2SO does, however, appear to form strong hydrogen bonds to imidazole. The FAB MS of this system in glycerol shows a peak at m/z 271, which can be assigned to a protonated imidazole-Ph_2SO hydrogen-bonded complex ion. The relative intensity of this peak is approximately one-half of the intensity of the corresponding (imidazole-phosphate + H^+) ion peak.

The observed crystal structure of the imidazole-phosphate complex is in excellent agreement with the structure deduced from the FAB MS data and is shown in Figure 1. The complex contains infinite chains of imidazole-$(MeO)_2PO_2H$ units. The two N-O distances are 2.68 (1) and 2.67 (1) Å, i.e., equal within experimental error, and the bond angles are 171.0 (4)° and 176.5 (4)°, which are consistent with the presence of strong NHO hydrogen bonds.

The successful application of FAB MS to the analysis of a hydrogen-bonded complex suggests that this technique may well become a routine analytical method for the study of strong hydrogen bonding.[4] The information obtained is complementary to that obtained from other "fast" analytical technqiues such as infrared and NMR spectroscopy. While FAB MS cannot provide the same detailed information as X-ray crystallography, it is a much simpler technique and it can be used to study liquids or solutions thus removing the need for a crystalline sample.

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Registry No. Ph_2O, 101-84-8; Ph_2CO, 119-61-9; Ph_2SO, 945-51-7; imidazole, 288-32-4; trimethyl phosphate, 512-56-1; dioxane, 123-91-1.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Copper-Dioxygen Chemistry. Synthesis, Spectroscopy, and Properties of a Copper(II) Superoxide Complex

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In this contribution, I present initial results on a copper-dioxygen adduct prepared by reaction of molecular oxygen with a Cu(I) complex having an easily displaced ligand. Analytical and spectroscopic data and physical properties suggest formation of a Cu(II)-superoxide complex. Bound dioxygen is displaced by small molecules such as carbon monoxide, acetonitrile, and ethylene. Copper-dioxygen adducts are often proposed as intermediates in Cu(I) autoxidation reactions but have not been previously isolated and characterized.[1,2] These adducts are generally unstable and rapidly decompose to hydrogen peroxide or other reduced oxygen species.[2] This study presents the first well-characterized example of reversible dioxygen binding by a copper complex.

The Cu(I)-ethylene complex $Cu(HB(3,5\text{-}Me_2(pz))_3)(C_2H_4)$ (I) $(HB(3,5\text{-}Me_2(pz))_3$ = hydrotris(3,5-dimethyl-1-pyrazolyl)-

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