1270 *Inorg. Chem.* **1982**, *21*, 1270–1272

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Electronic Spectrum of $[FeCl_5(H_2O)]^{2-}$

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Received July 30, 1981

Electronic ground-state properties of the compounds $A_2[FeCl_5(H_2O)]$ ($A = NH_4^+, K^+, Cs^+$) and their diluted analogues $A_2[In_{1-x}Fe_xCl_5(H_2O)]$ have been studied by various techniques. The ammonium and potassium salts of both indium and iron complexes are isostructural, crystallizing in space group *Pnma*.[1,2] $Cs_2[FeCl_5(H_2O)]$ is isostructural with $Cs_2[RuCl_5(H_2O)]$, space group *Cmcm*.[3] The three pure iron compounds exhibit interesting low-temperature magnetic properties. From heat capacity and magnetic susceptibility measurements they were shown to order antiferromagnetically at temperatures near 10 K.[3,4]

Very little is known about electronically excited states. Optical spectroscopic data on compounds containing $[FeCl_5(H_2O)]^{2-}$, and the related $[FeCl_6]^{3-}$, are scarce. Only diffuse reflectance powder spectra have been recorded, and their interpretations are controversial.[5-7] The main experimental difficulty in obtaining reliable transmission spectra in the region of d–d transitions lies in their low intensity. Crystals of several millimeters thickness produce optical densities of the order of 10^{-1}. The charge-transfer transitions to higher energy, on the other hand, are 4 orders of magnitude more intense. Their low-energy tail is the cause of the typical yellow-red color of the compounds. In the present study we investigate both d–d and charge-transfer excited states by low-temperature single-crystal absorption spectroscopy.

Experimental Section

Preparations. $Cs_2[FeCl_5(H_2O)]$, $K_2[FeCl_5(H_2O)]$, and $(NH_4)_2[FeCl_5(H_2O)]$ were prepared as described in the literature.[8,9] Large single crystals were obtained by slow evaporation of saturated solutions in a dry atmosphere.

Pale yellow crystals of $(NH_4)_2[InCl_5(H_2O)]$ doped with 3×10^{-2} mol % $[FeCl_5(H_2O)]^{2-}$ were found suitable for spectroscopic measurements in the UV region. They were obtained by dissolving NH_4Cl (2 parts), $InCl_3 \cdot 4H_2O$ (0.95 part), and $FeCl_3$ (0.05 part) in 1 M HCl. After a few days in a dry atmosphere the crystals could be separated.

All the compounds were characterized by elemental analysis and by X-ray diffraction.

Spectroscopic Measurements. The absorption spectra were measured on a Cary 17 spectrophotometer. A red-sensitive GaAs photocathode was used for measurements in the near-IR. The light was polarized by a matched pair of Glan–Taylor prisms. A helium flow-tube technique was used for cooling. Crystals were oriented with a polarizing microscope and a Buerger precession X-ray camera.

$Cs_2FeCl_5(H_2O)$. The $FeCl_5(H_2O)$ units are all aligned with their Fe–O axes parallel to *b* of the orthorhombic unit cell.[3] The water molecules lie in the *bc* plane, approximately parallel to σ_d of the coordination octahedron. The exact Fe site symmetry is C_{2v}. A large crystal was cleaved approximately parallel to {100}. Spectra were measured perpendicular to this face, with the electric vector parallel to *b* and *c*, the two extinction directions.

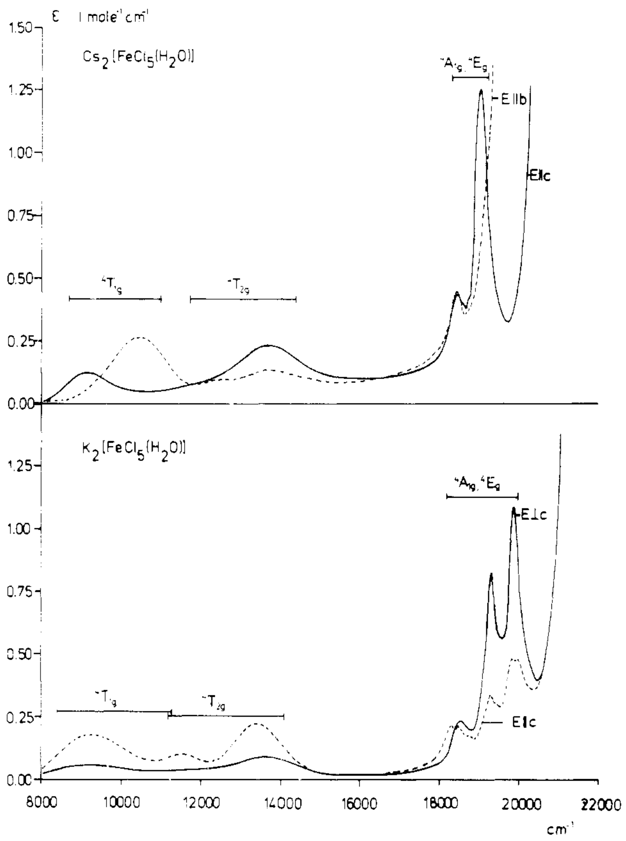

Figure 1. Polarized single-crystal absorption spectra of $Cs_2[FeCl_5(H_2O)]$ and $K_2[FeCl_5(H_2O)]$ ({210} face) in the region of d–d transitions (T = 12 K).

Table I. Band Positions, Intensities, and Predominant Polarizations of d–d Transitions[a]

$Cs_2[FeCl_5(H_2O)]$			$(NH_4)_2[FeCl_5(H_2O)]$			$K_2[FeCl_5(H_2O)]$		
	ϵ^c			ϵ^c			ϵ^c	
ν^b	$E \parallel b$	$E \parallel c$	ν^b	$E \parallel c$	$E \parallel b$	ν^b	$E \parallel c$	$E \perp c$
9 020		0.12	8 700	0.08		9 250	0.18	
10 500	0.25							
			11 360	0.07		11 470	0.09	
12 200	(sh)							
13 660	0.08	0.16	13 880	0.20	0.07	13 510	0.22	0.07
18 580	0.25	0.25	18 310	0.06	0.06	18 310	0.14	
18 690		(sh)	18 690	0.17	(sh)	18 480	0.15	0.15
18 860		(sh)	18 970	(sh)	(sh)	19 300	0.14	0.65
19 120		0.95				19 840	0.16	0.82
						19 960	(sh)	

[a] Spectra were measured perpendicular to {100} and {210} in $(NH_4)_2[FeCl_5(H_2O)]$ and $K_2[FeCl_5(H_2O)]$, respectively. Relations between crystal and molecular polarizations are given in eq 1. The listed ε values in the $^4A_{1g}$, ^4E_g region are corrected for the underlying charge-transfer absorption tail. [b] In cm^{-1}. [c] In L mol^{-1} cm^{-1}.

$(NH_4)_2[FeCl_5(H_2O)]$, $K_2[FeCl_5(H_2O)]$, and $(NH_4)_2[In_{1-x}Fe_xCl_5(H_2O)]$. In this crystal structure the molecular units are not aligned parallel.[1] The spectra measured along the extinction directions of the crystal are therefore, in general, a composition of more than one molecular polarization. The Fe site symmetry is C_s, and the water molecule lies within a σ_h plane of the coordination octahedron. Both {100} and {210} faces were used for experiments. There are the following relations between molecular and crystal polarizations:

$$\begin{aligned} &\{100\} \text{ face: } I(E \parallel b) = I_x;\ I(E \parallel c) = 0.50 I_y + 0.50 I_z \\ &\{210\} \text{ face: } I(E \parallel c) = 0.50 I_y + 0.50 I_z; \\ &\qquad I(E \perp c) = 0.67 I_x + 0.16 I_y + 0.16 I_z \end{aligned} \qquad (1)$$

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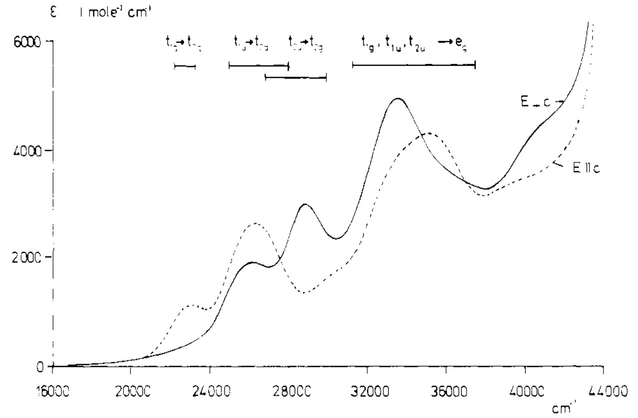

Figure 2. Polarized single-crystal absorption spectrum (at 12 K) of $[(NH_4)_2In_{1-x}Fe_xCl_5(H_2O)]$ in the region of charge-transfer transitions.

Table II. Band Positions, Intensities, and Predominant Polarizations of Charge-Transfer Transitions[a]

$(NH_4)_2[In_{1-x}Fe_xCl_5(H_2O)]$			$Cs_2NaY_{1-x}Fe_xCl_6$	
	ϵ^c			
ν^b	$E \parallel c$	$E \perp c$	ν^b	ϵ^c
23 040	800		22420	70
26 280	2600	1800	24 930	620
28 770		2000	27 930	580
33 370		4700	32 040	850
34 870	3900		34 830	640
39 200	(sh)		38 160	500
40 700		(sh)		

[a] The $(NH_4)_2[In_{1-x}Fe_xCl_5(H_2O)]$ spectrum was measured perpendicular to {210}. [b] In cm⁻¹. [c] In L mol⁻¹ cm⁻¹.

where, x, y, and z are defined as follows: z is parallel to Fe–O; x and y are parallel and perpendicular, respectively, to the plane defined by H_2O.

Results

Figure 1 shows absorption spectra of $Cs_2[FeCl_5(H_2O)]$ and $K_2[FeCl_5(H_2O)]$ in the region of d–d transitions. Band positions, intensities, and predominant polarizations for all the three compounds are summarized in Table I. The results are in agreement with independent measurements by McCarthy.[10]

Figure 2 shows the charge-transfer region in the absorption spectrum of $(NH_4)_2[In_{1-x}Fe_xCl_5(H_2O)]$. In Table II the band positions, intensities, and polarizations are compared with those of $Cs_2NaY_{1-x}Fe_xCl_6$.[11]

Discussion

d–d Transitions. From the general appearance of the absorption bands and a comparison with octahedral manganese(II) complexes the assignment of low-energy d–d transitions, as indicated in Figure 1, is straightforward. The $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ (O_h notation) transitions, which, in a strong-field approximation, are pure spin flips, are narrow compared to transitions to $^4T_{1g}$ and $^4T_{2g}$, which involve $t_{2g} \rightarrow e_g$ orbital jumps. At room temperature the ^4E_g, $^4A_{1g}$ bands cannot be observed due to the overlapping charge-transfer absorption. The splittings of $^4T_{1g}$ and $^4T_{2g}$ due to the substitution of an axial chloride ligand by water are of the order of 2000 cm⁻¹. Similar splittings were found in $[MnCl_4(H_2O)_2]^{2-}$.[12]

The observed differences in band positions and fine structure are the result of several physical effects. The ligand field anisotropy of $[FeCl_5(H_2O)]^{2-}$ is axial only to a first approximation. Iron to water π bonding introduces a rhombic component. The different orientation of the H_2O plane with respect to the coordination octahedron (cf. section on Spectroscopic Measurements) for the three compounds can therefore explain part of the spectroscopic differences. In addition $Cs_2[FeCl_5(H_2O)]$ on the one hand and $K_2[FeCl_5(H_2O)]$ and $(NH_4)_2[FeCl_5(H_2O)]$ on the other show pronounced differences of Fe–Cl interatomic angles and distances. The deviations from axial coordination are particularly pronounced in the latter structure. Besides these intramolecular effects, exchange coupling of nearest neighbors in the lattice affects the fine structure of $^4A_{1g}$, ^4E_g absorptions. The differences between the potassium and ammonium salts in this spectral range are thus a reflection of the different low-temperature magnetic properties.

Differences in band polarizations and intensity distributions between the three compounds are also quite pronounced. There are two main sources of intensity for the formally spin-forbidden d–d transitions: (i) spin–orbit coupling in conjunction with the low-symmetry ligand field (including vibronic interaction), (ii) exchange interactions between the magnetic centers in the lattice. On the basis of our experiments it is not possible to decide how the two mechanisms contribute to the intensities. The strong polarizations of most of the bands point to rather restrictive mechanisms. If the intensities are predominantly exchange induced, they must critically depend on exchange pathways. No definite conclusions concerning exchange pathways were reached in the magnetochemical investigations.[3,4] Except for some small features in the ^4E_g, $^4A_{1g}$ region of $(NH_4)_2[FeCl_5(H_2O)]$ our spectra did not show any discontinuous changes on crossing the Néel temperature. The magnetic phase transitions are thus not likely to be accompanied by drastic structural changes. Exchange-induced intensity mechanisms are not ruled out by this observation. Short-range rather than long-range order affects intensities. And short-range order usually extends to temperatures well above the Néel point.

Charge-Transfer Transitions. The general appearance of the spectrum is similar to that of $[FeCl_6]^{3-}$.[10] Band positions are slightly higher in $[FeCl_5(H_2O)]^{2-}$. The bands are more intense by a factor of approximately 3 and considerably broader. The absorptions in the range 22 000–36 000 cm⁻¹ can therefore safely be assigned to electron-transfer transitions from chloride-centered nonbonding and antibonding orbitals to metal-centered t_{2g} and e_g. For the bands around 40 000 cm⁻¹, which have no obvious counterparts in the $FeCl_6^{3-}$ spectrum, oxygen- as well as chloride-centered donor orbitals have to be considered. These results are in good agreement with Jørgensen's concept of optical electronegativity.[13] According to that model the energy (in cm⁻¹) of the first allowed ligand → metal electron-transfer band is

$$\nu = 30[\chi_{opt}(\text{ligand}) - \chi_{opt}(\text{metal})]$$

With estimated values of 3.0 and 3.5 for $\chi_{opt}(Cl)$ and $\chi_{opt}(H_2O)$, respectively, the first transitions involving oxygen-centered donor orbitals are expected to lie 15 000 cm⁻¹ above the first Cl → Fe transition. Splittings of the $^6T_{1u}$ (O_h notation) excited states due to the low symmetry may be estimated from the observed widths and a comparison with the $[FeCl_6]^{3-}$ spectrum: 2000–3000 cm⁻¹ for $t_{1u}, t_{2u} \rightarrow t_{2g}$ (O_h notation) transitions and 3000–5000 cm⁻¹ for $t_{1u}, t_{2u} \rightarrow e_g$ transitions.

Further splittings of excited states are caused by spin–orbit coupling. Since the excited states derive from three open-shell electron configurations, e.g. $(t_{1u})^5(t_{2g})^4(e_g)^2$ (O_h notation), three contributions to the spin–orbit coupling have to be considered. Of these $\zeta(e_g)$ can be neglected. Since the donor orbitals are almost pure ligand orbitals, $\zeta(t_{1u}) \approx \zeta(Cl) \approx 500$ cm⁻¹. Similarly $\zeta(t_{2g}) \approx \zeta(Fe) \approx 300$ cm⁻¹. Spin–orbit splittings of the

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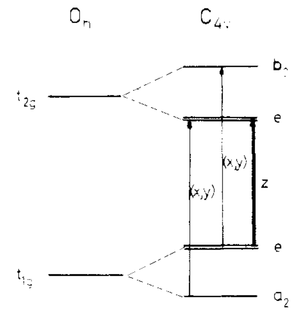

Figure 3. Schematic representation of the lowest energy charge-transfer transition in approximate C_{4v} symmetry.

order of several hundred wavenumbers are therefore expected. The observed bandwidths are too large to resolve them in the absorption spectrum.

Some of the absorption bands in Figure 2 show pronounced linear dichroism. The dichroism is particularly well resolved in the first band at 23 040 cm^{-1}, which we assign to the $t_{1g} \rightarrow t_{2g}$ (O_h notation) one-electron transition: it is polarized completely parallel to Fe–O. This may be rationalized as follows.

We assume idealized C_{4v} symmetry for the complex with z parallel to Fe–O. This is an approximation, since the complexes are, in reality, quite strongly distorted in the crystals.[1] Through the substitution of one axial chloride by oxygen, the t_{1g} and t_{2g} orbitals are split into tetragonal components as shown in Figure 3. There are three formally allowed one-electron transitions, two x, y polarized and one z polarized. From the relative disposition of donor and acceptor orbitals[14] it is easy to see that only one can acquire intensity in a ligand to metal charge-transfer mechanism: $e(t_{1g}) \rightarrow e(t_{2g})$. This transition is z polarized and has its origin in the predominant weight of p_x, p_y orbitals of the axial chloride (compared to the corresponding oxygen orbitals) in the donor $e(t_{1g})$ orbital. Dichroism is also observed in the higher energy part of the spectrum. But the situation is complicated by the excited-state splittings and the overlapping absorption bands.

Acknowledgment. We thank P. J. McCarthy for fruitful discussion and correspondence. The work was financially supported by the Swiss National Science Foundation (Grant No. 2.872-77).

Registry No. $Cs_2[FeCl_5(H_2O)]$, 25500-43-0; $(NH_4)_2[FeCl_5(H_2O)]$, 16774-56-4; $K_2[FeCl_5(H_2O)]$, 15132-22-6; $(NH_4)_2[InCl_5(H_2O)]$, 17949-59-6; $Cs_2Na[YCl_6]$, 27880-16-6; $Cs_2Na[FeCl_6]$, 28015-80-7.

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Bifunctional Activation of Coordinated Carbon Monoxide: A Kinetic Study of Lewis Acid Induced Alkyl Migration

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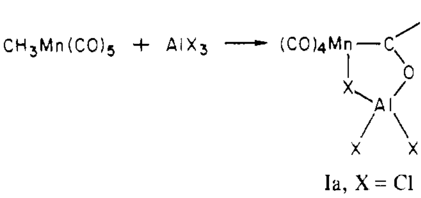
Received June 17, 1981

Table I. Kinetic Data for Reaction 1 at 22 °C

Lewis acid	solvent	[acid],[a] M	$[CH_3Mn(CO)_5]$,[a] M	k_{obsd}, s^{-1}
$AlBr_3$[b]	*n*-heptane	2.30×10^{-2}	9.55×10^{-4}	170[c]
$AlCl_3$[d]	benzene	6.55×10^{-4} [e]	5.65×10^{-3}	170[c]
$AlCl_2Et$[b]	*n*-heptane	1.20×10^{-2}	5.60×10^{-4}	10 ± 1[f,g]
$AlClEt_2$[b]	*n*-heptane	5.50×10^{-2}	4.04×10^{-4}	0.37 ± 0.02[f,g]

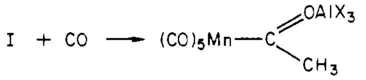
[a] Concentration after mixing. [b] Pseudo first order in acid. [c] Lower limit for k_{obsd}; see text. [d] Pseudo first order in $CH_3Mn(CO)_5$. [e] Saturated $AlCl_3$ in benzene; see ref 12. [f] Average of four or more determinations. [g] Redistribution of the alkylaluminum chloride takes places prior to insertion.

The alkyl migration (CO insertion) reaction of transition-metal complexes has been the subject of numerous synthetic and mechanistic investigations.[1] This transformation is of interest because it is a fundamental reaction of organometallic compounds as well as an important step in the commercial production of oxygenated hydrocarbons with use of transition-metal catalysts.[2] Recently we reported that molecular Lewis acids such as $AlBr_3$ induce rapid alkyl migration in $CH_3Mn(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, and $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$, forming cyclic adducts as seen in eq 1.[3] Upon


(1)

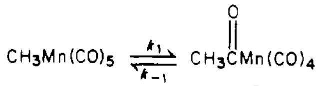
Ia, X = Cl
b, X = Br

exposure to subatmospheric pressures of CO, the cyclic complex I undergoes further reaction, eq 2, which has been the subject of a kinetic study.[3]



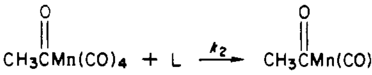
$$\mathrm{I} + CO \longrightarrow (CO)_5Mn{-}C(=OAlX_3)CH_3 \qquad (2)$$

A critical question in understaning reaction 1 is whether the Lewis acid facilitates the methyl migration or simply captures the coordinatively unsaturated intermediate II, which as shown in eq 3a appears to be formed in the conventional CO insertion



$$CH_3Mn(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3\overset{\overset{\displaystyle O}{\|}}{C}Mn(CO)_4 \qquad (3a)$$

II



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}Mn(CO)_4 + L \xrightarrow{k_2} CH_3\overset{\overset{\displaystyle O}{\|}}{C}Mn(CO)_4L \qquad (3b)$$

reaction.[1] Although II has never been directly observed, the kinetic evidence for its existence is strong.[1] Our previous work showed that the rate of reaction 1 was too rapid to measure by classical kinetic techniques.[3] In the present research, we have applied the much faster stopped-flow technique in the investigation of reaction 1.

Experimental Section

Kinetic runs were carried out at 22 °C with an Applied Photophysics Model 1705 stopped-flow spectrophotometer modified for work with air-sensitive compounds. Reactants were prepared and purified as previously described.[3] Solvents were dried by using Na/K alloy and degassed by multiple freeze–pump–thaw cycles on a high-vacuum line. The cyclic acetyl product I absorbs light in the near-UV region, whereas the starting materials are essentially transparent.[4] The

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