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Cationic Tetrahydrofuran-Aquo Transition Metal Complexes

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Interaction of hydrated 3d metal perchlorates with tetrahydrofuran (THF) in triethyl orthoformate leads to the formation of cationic THF-aquo metal complexes. These compounds were characterized by means of spectral, magnetic, conductance and X-ray powder diffraction studies. IR spectra established the presence of coordinated THF and aquo groups and ionic perchlorate in the new complexes. A distorted O_h *ligand field symmetry was assigned to complexes of the type* $[M(THF)_4(H_2O)_2]^{2,3+}$ *(M =* Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}*).* $[Cu(THF)_3(H_2O)]^{2+}$ *is essentially square planar and* $[Fe(THF)_3(H_2O)]^{2+}$ *has a distorted tetrahedral structure. In the latter complex the split (d–d) band occurs in the 900-1200 nm region, owing to the relatively strong ligand field generated by THF and aquo groups. The aquo groups are strongly bonded in the new complexes and cannot be removed by desiccation over a number of effective drying agents.*

Introduction

Complexes of tetrahydrofuran (THF) with various metal halides have been synthesized and studied in recent years.[1-9] 3d metal halides form the following complexes with THF (X = Cl, Br, I; n = 2-4):[1,2,4,7,8] $CuCl_2 . 0.8$ THF, MX_n . THF (M = Ti^{III}, Co^{II}), $NiCl_2$. THF . C_2H_5OH, MX_n . 1.5 THF (M = Mn^{II}, Fe^{II}, Co^{II}), MX_n . 2 THF (M = Ti^{II}, Ti^{IV}, V^{IV}, VO, Cr^{II}, Ni^{II}, Zn^{II}), MX_n . 3 THF (M = Ti^{III}, V^{III}, Cr^{III}). No information appears in the literature on cationic THF complexes, however. It was felt that a study in this direction was in order, and synthetic and characterization studies of THF-transition metal perchlorate complexes were undertaken. Interaction of hydrated metal perchlorates with THF in triethyl orthoformate leads to the formation of mixed ligand (THF-water) cationic complexes. The present paper deals with the synthesis and characterization of these compounds.

Experimental Section

Synthetic Procedure: THF (water content less than 0.05%) and the hydrated metal perchlorate are mixed separately with triethyl orthoformate and the resulting mixtures are warmed at 50°C for 15 min. The solution of THF is then added to that of the metal salt (molar ratio of THF to salt *ca.* 6:1) and the mixture is maintained at the above temperature, under continuous stirring, for 1-2 hours. The mixture is then allowed to cool and a large excess of THF-triethyl orthoformate solution is added to it. A crystalline precipitate is formed either immediately or by stirring the mixture at room temperature for 5-10 min. The complexes prepared by this procedure are insoluble in the parent ether and stable in the atmosphere. They were filtered, washed with THF and benzene, and dried iin an evacuated desiccator over $Mg(ClO_4)_2$, $CaCl_2$ or P_2O_5. The new complexes contain coordinated water as demonstrated by IR evidence (*vide infra*) and analytical data (C to H ratios), which cannot be removed even after prolonged desiccation over any of the above drying agents. Properties and analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.) of the new complexes are given in Table I.

Spectral, Magnetic, Conductance and X-ray Studies. IR spetra (Table II), electronic spectra (Table III, Figures 1-3) and magnetic and conductance measurements (Table IV) were obtained by procedures previously described.[10] A North American Phillips X-ray diffractometer was utilized for X-ray powder diffraction patterns (Cu–Kα radiation). d-values of the main peaks are given in Table V.

Results and Discussion

IR Spectra, Conductivities and X-ray Patterns. Complexes of the types $M(THF)_4(H_2O)_2(ClO_4)_n$ (M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}; n = 2, 3) and $M(THF)_3(H_2O)(ClO_4)_2$ (M = Fe^{II}, Cu^{II}) were obtained during the present work. The spectral, magnetic, conductance and X-ray data allow the characterization of these compounds. Conductance measurements establish that the divalent metal ion complexes are 2:1 elec-

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[1] R. J. Kern, *J. Inorg. Nucl. Chem.*, *24*, 1105 (1962).
[2] R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963).
[3] K. N. Semenenko and N. Ya. Turova, *Zhur. Neorg. Khim.*, *8*, 2093 (1963).
[4] B. E. Bridgland, G. W. A. Fowles, and R. A. Walton, *J. Inorg. Nucl. Chem.*, *27*, 383 (1965).
[5] K. Rossmanith and C. Auer-Welsbach, *Mh. Chem.*, *96*, 602, 607 (1965).
[6] K. Rossmanith, *ibid.*, *97*, 1357 (1966).
[7] G. W. A. Fowles, T. E. Lester, and R. A. Walton, *J. Chem. Soc.* (A), 1081 (1968).
[8] G. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Inorg. Nucl. Chem.*, *31*, 3119 (1969).
[9] K. Rossmanith, *Mh. Chem.*, *100*, 1484 (1969).
[10] (a) N. M. Karayannis, L. L. Pytlewski, and M. M. Labes, *Inorg. Chim. Acta*, 3, 415 (1969); (b) N. M. Karayannis, C. M. Paleos, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, *8*, 2559 (1969).

Table I. Analyses and Properties of Tetrahydrofuran Metal Complexes

Complex	Color	M.p. °C	Analysis C% Calcd.	C% Found	H% Calcd.	H% Found	Metal% Calcd.	Metal% Found
$[Mn(THF)_4(H_2O)_2](ClO_4)_2$	white	244-245, *d*	33.23	33.64	6.27	6.38	9.50	10.01
$[Fe(THF)_3(H_2O)](ClO_4)_2$	cream white	125-126, *d*	29.47	29.72	5.36	5.52	11.41	11.40
$[Fe(THF)_4(H_2O)_2](ClO_4)_3$	light yellow	135-136, *d*	28.32	28.45	5.35	5.90	8.23	8.45
$[Co(THF)_4(H_2O)_2](ClO_4)_2$ [a]	pink violet	109-110	33.00	33.48	6.23	6.36	10.12	10.82
$[Ni(THF)_4(H_2O)_2](ClO_4)_2$	light green	117-118.5	33.02	33.37	6.23	6.13	10.09	10.36
$[Cu(THF)_3(H_2O)](ClO_4)_2$	light blue	129-130, *d*	29.01	29.07	5.86	5.50	12.79	13.10
$[Zn(THF)_4(H_2O)_2](ClO_4)_2$	white	79-80	32.64	32.69	6.16	6.34	11.10	11.47

d, decomposes upon melting. [a] The Co^{II} complex contains 12.52% Cl (Calcd. 12.18%).

Table II. Infrared Data of Tetrahydrofuran Metal Complexes (cm^{-1})

Complex	Ionic ν_3	ClO_4^- ν_4	ν_{C-O-C} [a] (asymmetric & symmetric)	OH_2 rock	OH_2 wag	ν_{M-O} (M—THF and M—OH_2)
$[Mn(THF)_4(H_2O)_2](ClO_4)_2$	1092 vs	615 s	1010 s, sh, 960 m, 926 m, 840 s	670 m, b	552 s	390 m, b
$[Fe(THF)_3(H_2O)](ClO_4)_2$	1078 vs	615 m-s	1008 s, sh, 960 m, 925 s, 862 s	700 s [b]	585 s, sh	452 m, 397 m
$[Fe(THF)_4(H_2O)_2](ClO_4)_3$	1089 vs	613 m	1018 s, sh, 960 m, 948 m, 775 s	750 s	550 s	488 m, 464 m, b
$[Co(THF)_4(H_2O)_2](ClO_4)_2$	1065 vs	611 vs	1020 s, sh, 960 s, sh, 914 s, 844 s, b	670 m	548 s	400 m, 352 m
$[Ni(THF)_4(H_2O)_2](ClO_4)_2$	1070 vs	616 vs	1020 s, sh, 960 s, sh, 916 s, 869 s	747 s	650 m-s, sh	389 m, 368 m
$[Cu(THF)_3(H_2O)](ClO_4)_2$	1066 vs	617 vs	1022 s, sh, 970 s, sh, 934 s, 918 s, 848 vs	[c]	556 s	448 s, 400 s, sh
$[Zn(THF)_4(H_2O)_2](ClO_4)_2$	1074 vs	608 s	1016 s, sh, 988 s, b, 922 s, 846 s	644 s, sh	530 s, sh	365 m, b

[a] In free THF ν_{C-O-C} occurs at 1069 (asym.) and 909 (sym.) cm^{-1}.[4] [b] A shoulder (unassigned) is observed at *ca.* 650 cm^{-1} in the Fe^{II} complex. [c] Overlaps with the ν_{C-O-C} bands.

Table III. Electronic Spectra of Tetrahydrofuran Metal Complexes

Complex	Medium	λ, nm (ε_{max})
$[Mn(THF)_4(H_2O)_2](ClO_4)_2$	Nujol	259 vs
	1.7×10^{-2} *M* in CH_3NO_2	<370(>20)
$[Fe(THF)_3(H_2O)](ClO_4)_2$	Nujol	<300 vs, 916 s, sh, 1197 m, sh
	1.3×10^{-2} *M* in CH_3NO_2	<380(>150), 924(5)
	1.3×10^{-2} *M* in 0.1 *M* solution of THF in CH_3NO_2	<380(>150), 929(4.5)
$[Fe(THF)_4(H_2O)_2](ClO_4)_3$	Nujol	345 vs
	CH_3NO_2	<380(>1500)
$[Co(THF)_4(H_2O)_2](ClO_4)_2$	Nujol	454 s, 492 s, 544 s, 746 sh, 947 sh, 1184 m, 1426 m
	2.5×10^{-2} *M* in CH_3NO_2	468 sh, 484(19), 1164(3.7), 1412(1.6)
	2.5×10^{-2} *M* in 0.1 *M* solution of THF in CH_3NO_2	465 sh, 487(17), 514(16), 1140 b (4.8)
$[Ni(THF)_4(H_2O)_2](ClO_4)_2$	Nujol	401 s, 680 sh, 747 s, 753 sh, 1196 m, 1434 m
	5×10^{-2} *M* in CH_3NO_2	393(9), 648(4.4), 722 sh (3.3), 1086(3.7), 1176(3.5), 1412(1.4)
	5×10^{-2} *M* in 0.1 *M* solution of THF in CH_3NO_2	397(8.5), 664(4.2), 724 sh (3.9), 1111(3.7), 1138 sh (3.6)
$[Cu(THF)_3(H_2O)](ClO_4)_2$	Nujol	<300 s, 734 m, b
	7.5×10^{-3} *M* in CH_3NO_2	<380(>55), 738(10.8)
	7×10^{-3} *M* in 0.1 *M* solution of THF in CH_3NO_2	<380(>30), 773(10), 911(7.1), 996 sh (4)

s, strong; m, medium; v, very; b, broad; sh, shoulder.

trolytes in nitromethane and that of Fe^{III} is a 3:1 electrolyte (Table IV). IR spectra indicate that only ionic (T_d) perchlorate groups are present in these complexes[11] (Table II). Although coordination of perchlorate does not necessarily lead to splittings of the vibrational modes of this group,[12] the presence of coordinated perchlorato groups in the complexes reported can be ruled out. In fact, the solid state electronic spectra of the new complexes (Table III), which are discussed later in the text, and their far IR spectra indicate that the metal ion is hexacoordinated in

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(11) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961); B. J. Hathaway, D. G. Holah, and M. Hudson, *ibid.*, 4586 (1963).

(12) A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *Inorg. Chim. Acta*, 2, 195 (1968).

Table IV. Magnetic Moments at 296°K and Electrical Conductivities (10^{-3} *M* Nitromethane Solutions at 25°C) of Tetrahydrofuran Metal Complexes

Complex	$\chi_M^{corr} \times 10^6$, cgsu	μ_{eff}, BM	Λ_M, ohm^{-1} cm^2 mole^{-1}
$[Mn(THF)_4(H_2O)_2](ClO_4)_2$	15,400	6.06	154
$[Fe(THF)_3(H_2O)](ClO_4)_2$	12,097	5.37	178
$[Fe(THF)_4(H_2O)_2](ClO_4)_3$	14,864	5.96	211
$[Co(THF)_4(H_2O)_2](ClO_4)_2$	8,978	4.63	166
$[Ni(THF)_4(H_2O)_2](ClO_4)_2$	4,448	3.26	164
$[Cu(THF)_3(H_2O)](ClO_4)_2$	1,290	1.76	171
$[Zn(THF)_4(H_2O)_2](ClO_4)_2$	Diamagnetic		152

Table V. X-ray Powder Diffraction Data of Tetrahydrofuran Metal Complexes

Complex	d-Spacings (Å)
$[Mn(THF)_4(H_2O)_2](ClO_4)_2$	12.99, 11.33, 10.64, 9.93, 8.42, 6.86, 6.28, 5.12, 4.37, 4.17, 3.93, 2.80
$[Fe(THF)_3(H_2O)](ClO_4)_2$	13.18, 11.62, 10.52, 9.21, 8.34, 4.40, 5.21, 4.72, 4.33, 4.13, 4.04, 3.97, 3.86, 3.42, 3.14, 2.77
$[Fe(THF)_4(H_2O)_2](ClO_4)_3$	12.99, 11.62, 10.52, 9.82, 8.42, 6.96, 6.32, 5.06, 4.34, 4.22, 3.95, 2.81
$[Co(THF)_4(H_2O)_2](ClO_4)_2$	12.10, 11.04, 10.04, 9.21, 8.50, 7.02, 6.28, 5.68, 4.98, 4.67, 4.27, 4.04, 3.75, 2.79
$[Cu(THF)_3(H_2O)](ClO_4)_2$	18.39, 14.71, 11.62, 10.64, 6.91, 5.90, 4.82, 4.11, 3.98, 3.85, 3.34
$[Zn(THF)_4(H_2O)_2](ClO_4)_2$	13.59, 11.94, 10.52, 9.82, 8.42, 6.96, 6.32, 5.06, 4.33, 4.17, 3.88, 2.79

$M(THF)_4(H_2O)_2(ClO_4)_n$ and tetracoordinated in $M(THF)_3(H_2O)(ClO_4)_2$. The complexes are, thus, formulated as $[M(THF)_4(H_2O)_2](ClO_4)_{2,3}$ (M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}) and $[M(THF)_3(H_2O)](ClO_4)^2$ (M = Fe^{II}, Cu^{II}).

Coordination of THF is demonstrated by the IR spectra of the new complexes.[2,4,8] In fact, the symmetric ν_{C-O-C} vibration, which occurs at 909 cm^{-1} in free THF,[4] splits into several bands in the complexes (Table II), as is also the case with $VCl_4 . 2\,THF$.[4] The asymmetric ν_{C-O-C} band, occurring at 1069 cm^{-1} in free THF,[4] overlaps considerably with the very strong ν_3 band of ionic perchlorate and appears as a shoulder (Table II). Coordinated water bands at 3550-3400 (ν_{OH}) and 1630-1600 (δ_{H-O-H}) cm^{-1} [13] appear in all the complexes reported. In the region below 1000 cm^{-1} the characteristic rocking and wagging modes of coordinated water are observed.[14] Tentative assignments of these bands, given in Table II, agree in most cases with the frequencies calculated by Nakagawa and Shimanouchi for these vibrations.[14] Below 500 cm^{-1} bands attributable to ν_{M-O} modes are observed. Fowles *et. al.* reported that the far IR spectra of transition metal halide-THF complexes exhibit wide differences and did not make assignments of ν_{ligand} and ν_{M-O} bands.[8] Only a weak band at 390 cm^{-1} was common in these complexes, while ν_{M-Cl} bands were identified, in certain cases, in the 340-255 cm^{-1} region.[8] In the cationic complexes reported here, bands at 490-350 cm^{-1} may be tentatively assigned as primarily ν_{M-O} (THF) and ν_{M-O} (OH_2) (Table II), since they are in agreement with the formulation of these compounds discussed above. In fact, these bands occur at higher frequencies in the two tetracoordinated (Fe^{II} and Cu^{II}) complexes and that of Fe^{III}, as would be expected.[12,15]

The X-ray powder patterns of the Mn^{II}, Fe^{III} and Zn^{II} complexes are very similar and these compounds are of about the same structure. The Co^{II} complex exhibits a considerably different pattern. The Ni^{II} complex tends to collapse to an oil during grinding and its X-ray pattern was not obtained. The patterns of the two tetracoordinated complexes are distinctly different (Table V).

Electronic Spectra and Magnetic Moments. The hexacordinated cationic metal complexes are of the general type $[ML_4X_2]^{n+}$ (L = THF, X = H_2O). The splittings observed in the (d–d) bands of the solid state electronic spectra of the Co^{II} (Figure 1) and Ni^{II} (Figure 2) complexes demonstrate that the metal ions are in a ligand field with distorted octahedral symmetry.[16,17] The magnetic moment of the Co^{II} complex is below the « octahedral » region for this metal ion and indicative of significant deviation from pure O_h symmetry.[16-19] In fact, the presence of lower symmetry components in octahedral Co^{II} complexes leads to magnetic moments closer to the spin-only value, owing to a loss in orbital degeneracy of the ground state of the Co^{II} ion (*e.g.* $^4T_{1g}(O_h) \rightarrow {}^4A$, $2\,^4B$ in C_2 symmetry).[18] In nitromethane the main visible band of the Co^{II} complex occurs at some 2300 cm^{-1} higher in energy, probably due to dissociation of the complex and subsequent solvation of the resulting species (Table III, Figure 1). Addition of excess THF to nitromethane solutions of the Co^{II} complex leads to the appearance of a shoulder at 514 nm (Table III), which may be interpreted in terms of an equilibrium between $[Co(THF)_4(H_2O)_2]^{2+}$ and the solvation product.

The magnetic moment of the Ni^{II} complex (Table IV) is within the octahedral region for Ni^{II}. Since the ground state of octahedral Ni^{II} compounds is non-degenerate, the effect of distortion on the ma-

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(13) I. Gamo, *Bull. Chem. Soc. Japan*, *34*, 760 (1961).

(14) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, *20*, 429 (1964).

(15) C. V. Berney and J. H. Weber, *Inorg. Chem.*, *7*, 283 (1968).

(16) W. Byers, A. B. P. Lever, and R. V. Parish, *Inorg. Chem.*, *7*, 1835 (1968).

(17) D. M. L. Goodgame, M. A. Hitchman, D. F. Marsham, and C. E. Souter, *J. Chem. Soc. (A)*, 2464 (1969).

(18) A. B. P. Lever, *Inorg. Chem.*, *4*, 1042 (1965).

(19) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *ibid.*, 2, 1162 (1963); F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, *85*, 2402 (1963).

gnetic moments is not so obvious.[16] Dissociation of this complex and solvation of the resulting species occurs, presumably, in nitromethane, as indicated by the shift of the (d–d) bands toward higher energies and the reversal of the relative intensities of the bands in the 600-800 nm region (Table III, Figure 2). In nitromethane solutions of this complex, containing excess THF, the (d–d) bands are again shifted toward lower frequencies and the difference in intensity between the 600-800 nm bands is diminished, probably due to an equilibrium between $[Ni(THF)_4(H_2O)_2]^{2+}$ and the solvation product, under these conditions.

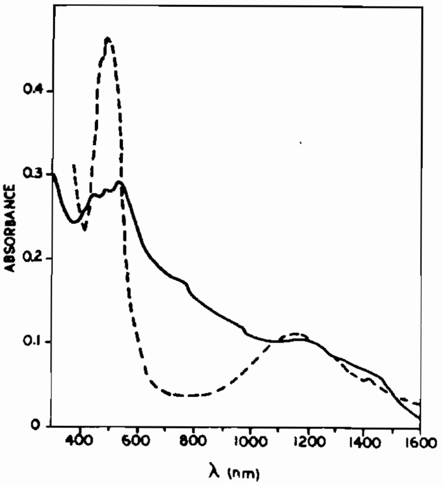

Figure 1. Electronic spectra of $[Co(THF)_4(H_2O)_2](ClO_4)_2$: (————), Nujol mull (absorbance, arbitrary scale) and (— — — —), 2.5×10^{-2} *M* in nitromethane.

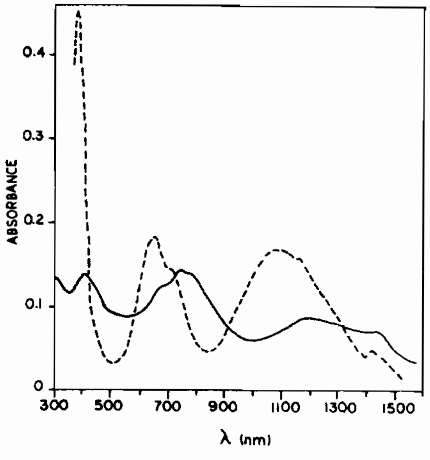

Figure 2. Electronic spectra of $[Ni(THF)_4(H_2O)_2](ClO_4)_2$: (————), Nujol mull (absorbance, arbitrary scale) and (— — — —), 5×10^{-2} *M* in nitromethane

A distorted octahedral structure is also assigned to the Mn^{II}, Fe^{III}, and Zn^{II} complexes, which are of about the same structure (Table V). The fact that the Co^{II} complex is not isomorphous to these compounds is probably due to differences in the extent of deviation from pure O_h symmetry.

The two tetracoordinated complexes are not isostructural. The solid state electronic spectrum of the Cu^{II} complex (Table III, Figure 3) exhibits the (d–d) band at 734 nm and may be assigned an effective symmetry lower than D_{4h} with a planar CuO_4 moiety.[16] The complex is apparently stable in nitromethane, but in the presence of excess ligand species with higher coordination number exist in solution as indicated by the shift of the maximum of the main (d–d) band toward lower energy and the appearance of two shoulders at 911 and 996 nm (Table III, Figure 3). This spectrum may be attributed to the presence of both penta- and hexa-coordinated cationic complexes of the types $[Cu(THF)_4(H_2O)]^{2+}$ and $[Cu(THF)_5(H_2O)]^{2+}$, under these conditions.

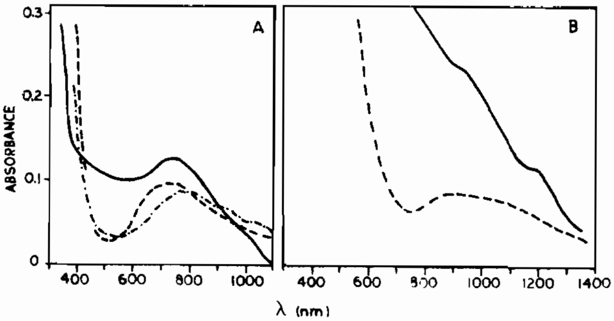

Figure 3. Electronic spectra of: (A) $[Cu(THF)_3(H_2O)](ClO_4)_2$: (————), Nujol mull, (— — — —), 7.5×10^{-3} *M* in nitromethane, (—·—·—·—), 7×10^{-3} *M* in 0.1 *M* THF solution in nitromethane; (B) $[Fe(THF)_3(H_2O)](ClO_4)_2$; (————), Nujol mull, (— — — —) 1.3×10^{-2} *M* in nitromethane. *The absorbance scale is arbitrary for the mull spectra.*

Tetracoordinated Cu^{II} compounds are common, but the stabilization of a Fe^{II} analog of $[Cu(THF)_3(H_2O)]^{2+}$ was rather unexpected. Fe^{II} generally forms cationic complexes with various monodentate ligands, having the same coordination number as the Mn^{II}, Co^{II}, Ni^{II} or Zn^{II} analogs (*e.g.* $[ML_6]^{2+}$ complexes with pyridine N-oxides[20] and sulfoxides[21]). Attempts at the isolation of $[Fe(THF)_4(H_2O)_2](ClO_4)_2$ by variation of the synthetic procedure were unsuccessful, however, and in all cases $[Fe(THF)_3(H_2O)](ClO_4)_2$ was precipitated. A square planar configuration can be imposed on Fe^{II} only as a result of special steric and electronic effects.[10a,22]

The solid state elctronic spectrum of the Fe^{II} complex (Table III, Figure 3) may be interpreted in terms of a distorted tetrahedral ligand field symmetry. The bands at 916 and 1197 nm are, presumably, due to the splitting of the $^5E \rightarrow {}^5T_2$ (in pure T_d) transition in a distorted tetrahedral ligand field.[23] This assignment leads to a Δ_t value of 9000-10500 cm^{-1}, which is close to that estimated for β-ketoenolato groups toward Fe^{II} (10000-12000 cm^{-1}).[23] Aquo and β-ketoenolato groups give rise to ligand fields of compa-

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(20) R. G. Garvey, J. H. Nelson, and R. O. Ragsdale, *Coordin. Chem. Rev.*, 3, 375 (1968).

(21) W. F. Currier and J. H. Weber, *Inorg. Chem.*, 6, 1539 (1967).

(22) A. B. P. Lever, *J. Chem. Soc.*, 3512 (1961); J. Chatt and B. L. Shaw, *ibid.*, 285 (1961); R. G. Burns, M. G. Clark, and A. J. Stone, *Inorg. Chem.*, 5, 1268 (1966).

(23) D. H. Gerlach and R. H. Holm, *ibid.*, 8, 2292 (1969).

rable strength.[24] THF, on the other hand, is a slightly stronger ligand than methanol,[25] whose position in the spectrochemical series is very close to that of the aquo groups (Dq toward octahedral Ni^{II}: CH_3OH 843 cm^{-1}, H_2O 860 cm^{-1}).[26] Thus, THF and aquo groups would be expected to generate a relatively strong tetrahedral ligand field, leading to the occurrence of the (d–d) bands in the Fe^{II} complex in the 900-1200 nm region.[23] The spectra of the Fe^{II} complex in nitromethane and in the presence of excess THF exhibit a broad band with its maximum at 924-929 nm. No conclusion can be drawn from these spectra, since distorted T_d,[23] penta- and hexa- coordinated Fe^{II} compounds exhibit the (d–d) bands in the 900-1200 nm region.

In conclusion, a number of mixed ligand, THF-aquo, cationic complexes with d^5–d^{10} metal ions were synthesized by interaction of hydrated metal perchlorates and THF in triethyl orthoformate, a dehydrating agent.[27] Aquo groups apparently form strong covalent bonds with the metal ion and cannot be removed even after prolonged desiccation over a number of effective drying agents. Our experience during previous studies[28] and the present work suggests that the dehydration of hydrated metal perchlorates in triethyl orthoformate occurs in several stages. In fact, the formation of the complexes reported may be attributed to the interaction of metal perchlorate dihydrates or monohydrates with THF, under the experimental conditions.

The isolation of water-free cationic metal complexes of THF would probably require strictly anhydrous experimental conditions, in view of the similar donor strengths of aquo and THF ligands (*vide supra*). Attempts at the isolation and characterization of anhydrous cationic complexes of THF and other heterocyclic ethers are currently in progress at this laboratory. As is the case with pyrazole,[29] THF might be expected to form complexes of the type $[M(THF)_6]^{2,3+}$ under anhydrous conditions.

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(24) J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, *84*, 24 (1962); T. S. Piper and R. L. Carlin, *Inorg. Chem.*, *2*, 260 (1963).

(25) P. E. Rakita, S. J. Kopperl, and J. P. Fackler, Jr., *J. Inorg. Nucl. Chem.*, *30*, 2139 (1968).

(26) V. Imhof and R. S. Drago, *Inorg. Chem.*, *4*, 427 (1965).

(27) P. W. N. M. van Leeuwen and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.*, *3*, 145 (1967).

(28) N. M. Karayannis, C. Owens, L. L. Pytlewski, and M. M. Labes, *J. Inorg. Nucl. Chem.*, *31*, 2767 (1969).

(29) N. A. Daugherty and J. H. Swisher, *Inorg. Chem.*, *7*, 1651 (1968).