Table III

Rates of Solvolysis of *cis*-[Co(tren)Br₂]⁺ in Nonaqueous Solvents under Various Conditions (420 mμ)

[Complex], mM	Solvent	Temp, °C	Added electrolyte	Ionic strength, M	k_1, sec⁻¹
0.58[a]	DMSO	40.0	None	5.8×10^{-4}	3.20×10^{-3}
0.96	DMSO	40.0	None	9.6×10^{-4}	3.29×10^{-3}
3.20	DMSO	55.0	None	3.2×10^{-3}	1.37×10^{-2}
0.65	DMSO	55.0	None	6.5×10^{-4}	1.40×10^{-2}
3.30[b]	DMF	40.0	None	3.3×10^{-3}	2.40×10^{-3}
1.20	DMF	40.0	None	1.2×10^{-3}	2.43×10^{-3}
3.40	DMF	55.0	None	3.4×10^{-3}	1.07×10^{-2}
1.50	DMF	55.0	None	1.5×10^{-3}	1.05×10^{-2}
1.50[c]	NMF	25.0	None	1.5×10^{-3}	2.50×10^{-1}
2.00[d]	Formamide	25.0	None	2.0×10^{-3}	2.70×10^{-2}
1.00	DMSO	40.0	0.02 M Mg(ClO₄)₂	6.0×10^{-2}	3.10×10^{-3}
1.00	DMSO	40.0	0.10 M Mg(ClO₄)₂	3.0×10^{-1}	3.16×10^{-3}
1.00	DMSO	40.0	0.20 M Mg(ClO₄)₂	6.0×10^{-1}	3.35×10^{-3}
1.00	DMSO	40.0	0.005 M NaCl	6.0×10^{-3}	3.38×10^{-3}
1.00	DMSO	40.0	0.05 M NaCl	5.0×10^{-2}	5.10×10^{-3}
1.00	DMF	40.0	0.02 M Mg(ClO₄)₂	6.0×10^{-2}	2.35×10^{-3}
1.00	DMF	40.0	0.10 M Mg(ClO₄)₂	3.0×10^{-1}	2.38×10^{-3}
1.00	DMF	40.0	0.001 M NaCl	2.0×10^{-3}	2.50×10^{-3}
1.00	DMF	40.0	0.01 M NaCl	6.0×10^{-2}	4.25×10^{-3}

[a] k_1 at 670 mμ for DMSO = 3.26×10^{-3} sec⁻¹. [b] k_1 at 670 mμ for DMF = 2.42×10^{-3} sec⁻¹. [c] $k_2 = 6.8 \times 10^{-5}$ sec⁻¹. [d] $k_2 = 6.3 \times 10^{-5}$ sec⁻¹.
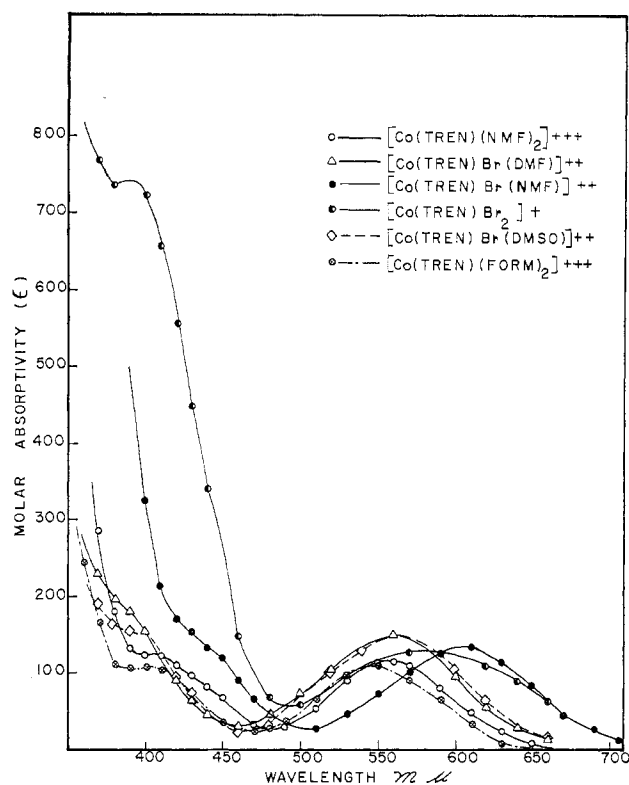

Figure 1.—Visible spectra of *cis*-[Co(tren)Br₂]⁺, *cis*-[Co(tren)-Br(solv)]²⁺ (where solv = DMF, NMF, or DMSO), and *cis*-[Co(tren)(solv)₂]³⁺ (where solv = NMF or formamide).

the product is formed. Quinn and Garner[13] have reported similar results for *cis* isomers of chromium(III) complexes. The solvolysis product in the present study must assume *cis* configuration because the steric property of the dibromo(triaminotriethylamine)cobalt-(III) cation is fixed, since the tertiary nitrogen atom must be *trans* to bromo or a solvent molecule. The electronic absorption spectra certainly indicate a *cis*

(13) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

configuration for various species (Figure 1). Therefore, it is quite reasonable to assume that the stereospecific rule for *cis* complexes in this case is also followed.

Langford[6] observed a significant decrease in the solvolysis rates in DMSO and DMF, as compared to the aquation rate of the *trans*-[Co(en)₂Cl₂]⁺ cation. This observation is consistent with results obtained in the present study for *cis*-[Co(tren)Br₂]⁺. Furthermore, a comparison of the relative solvolysis rates (aquation rate 1.0) at 35° of *trans*-[Co(en)₂Cl₂]⁺ in DMSO (0.31) and DMF (0.05) and of *cis*-[Co(tren)-Br₂]⁺ in DMSO (0.022) and DMF (0.015) seems to support the notion that solvolysis in nonaqueous, coordinating solvents is not basically different from solvolysis in water. The rates are altered but only moderately.[6]

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The Magnetic Susceptibilities of Erbium–Tellurium Intermediate Phases[1]

By J. Hoggins and H. Steinfink

The Er–Te system contains an intermediate stoichiometric compound ErTe₃ and a second intermediate phase which displays a solid solubility range

whose terminal compositions are ErTe and Er_2Te_3.[2] The latter has a cubic substructure which is isostructural with sodium chloride although its true crystal structure is orthorhombic with a large unit cell.[2] The pseudo-cubic lattice constant a_0 displays a sharp jump in its value near the composition Er_3Te_4. Electrical resistivity measurements on various compositions had shown that the number of carriers present was directly related to the concentration of erbium atoms and that the composition Er_2Te_3 had the most semiconducting behavior while ErTe displayed almost semimetallic conductivity.[3] Because of the abrupt change in lattice constant and the continuous variation of conductivity over a wide range of composition, we decided to investigate the magnetic susceptibility for several compositions in order to learn whether the introduction of additional erbium atoms into the structure produces a cooperative phenomenon among the unpaired spins in the solid.

Experimental Section

The magnetic susceptibility measurements were made by the Faraday method over the range 1.7°K to room temperature. Samples ranging from 2 to 10 mg were placed in a Pyrex sample bucket and suspended in an inhomogeneous field produced by a 4-in. electromagnet. The vertical forces exerted on the specimens were measured with a Cahn R-G electrobalance. Corrections for the sample holder were determined in advance and applied in each case. Measurements were made at several field strengths varying between 5 and 8 kG. The system was checked by measuring the magnetic susceptibility of $HgCo(CNS)_4$ and the known susceptibility for this compound was used to calculate the product HdH/dz at different current settings. The magnetic susceptibility of elemental erbium and tellurium were also measured at room temperature to serve as a check on the starting materials. Tellurium was diamagnetic with $\chi = -38.3 \times 10^{-6}$ emu/mol and erbium metal had $\chi = 47,167 \times 10^{-6}$ emu/mol in agreement with the values reported in the "Handbook of Chemistry and Physics," 45th ed. The compounds were prepared as previously described.[2] No correction was made for the diamagnetic contribution to the susceptibility of the compounds since they were strongly paramagnetic.

Results and Discussion

Figure 1 illustrates a representative curve of a plot of inverse magnetic susceptibility *vs.* temperature for one of the compositions investigated. All compounds showed paramagnetic behavior and no anomaly was observed in the range of compositions in which the pseudo-cubic lattice constant shows an abrupt change. Table I summarizes the magnetic properties for the compositions. The effective moment can be considered the same within experimental error and is in agreement with the theoretical moment 9.6 BM calculated for erbium in the ground state, $I_{15/2}$.

The compound ErTe had been investigated previously by Iandelli,[4] who reported $\theta = -12°K$, χ_M (298°K) = 34,965 $\times$ 10^{-6} emu/mol, and $\mu_{eff} = 9.30$ BM, in good agreement with the values shown in Table I. No magnetic ordering was observed for this compound over the temperature range 2.25–297°K
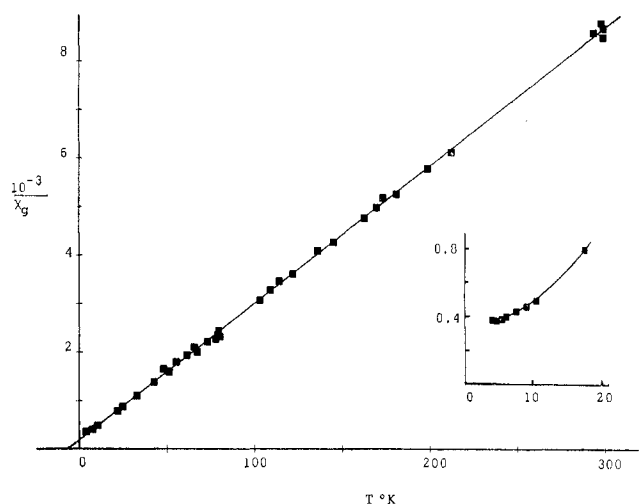
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Figure 1.—Plot of $1/\chi$ *vs.* T for the $ErTe_{1.15}$ composition in the solid solution region $ErTe-Er_2Te_3$. The data are characteristic of the behavior of the other phases investigated and listed in Table I.

TABLE I

MAGNETIC PROPERTIES OF THE Er–Te INTERMEDIATE ALLOYS[a]

Alloy	$10^6 \chi_g$ (24°), emu/g	θ, °K	μ_{eff}, BM
ErTe	120.85 (1.53)	−9	9.35 ± 0.14
$ErTe_{1.15}$	116.48 (1.47)	−6	9.39 ± 0.14
$ErTe_{1.20}$	118.39 (1.49)	−8	9.45 ± 0.14
$ErTe_{1.30}$	106.06 (1.34)	−2	9.24 ± 0.14
$ErTe_{1.33}$	102.84 (1.29)	0	9.18 ± 0.14
$ErTe_{1.50}$	103.73 (1.31)	−3	9.50 ± 0.14
$ErTe_3$	66.02 (0.83)	−3	9.35 ± 0.14
α-$ErSe_2$	109.60 (1.38)	−3	9.33 ± 0.14
Er	282 (3.5)	. . .	. . .
Te	−0.30 (0.05)	. . .	. . .

[a] Numbers in parentheses indicate the errors in the values of χ and μ_{eff}.

although at very low temperatures the curve tends to become flat. This temperature-independent susceptibility is probably Van Vleck paramagnetism caused by the separation of energy levels much greater than kT. The compositions $ErTe_{1.15}$, $ErTe_{1.2}$, and $ErTe_{1.3}$ display behavior similar to that of ErTe. The composition $ErTe_{1.33}$, representing the composition where the pseudo-cubic lattice constant changes most rapidly, has the lowest value for the effective moment and also has $\theta = 0°K$, *i.e.*, it follows the Curie rather than the Curie–Weiss curve. In view of the small variations of θ for the various compositions, it is difficult to ascribe quantitative significance to it but it may indicate that in Er_3Te_4 any weak interactions, which may be present in other compositions, have completely disappeared. The stoichiometric compound $ErTe_3$ behaves very much like the other alloys indicating that the erbium in this phase is also present in the trivalent ground state. The magnetic susceptibility of α-$ErSe_2$ was investigated to see whether a change in the nonmagnetic ion has any influence on the susceptibility, and, as can be seen, none is observed. On the basis of these results, it must be concluded that the

deep-lying 4f orbitals are unaffected by the introduction of additional erbium ions into the crystal structure, and no interactions giving rise to ordering effects are observed.

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Dihalobis(triarylphosphine)iron(II) Complexes. Isotropic Proton Magnetic Resonance Shifts and the Kinetics of Ligand Exchange[1]

By Louis H. Pignolet, Denis Forster,
and William DeW. Horrocks, Jr.

A number of recent publications have dealt with the structure,[2] spectral and magnetic properties,[3,4] proton magnetic resonance spectra,[5-9] and ligand-exchange kinetics[10,11] of the pseudo-tetrahedral complexes of the type $M(TAP)_2X_2$, where TAP is triarylphosphine, M is Co(II) or Ni(II), and X is a halogen. We report here a study of the analogous iron(II) compounds. Complexes of this type were first reported by Naldini;[12] however, numerous synthetic attempts in two different laboratories failed to yield the desired compounds using her method. Instead they were prepared by a slight modification of the method by which Booth and Chatt[13] obtained bis(phosphine) complexes of iron(II) chloride.

Experimental Section

Dichlorobis(triphenylphosphine)iron(II).—Water was azeotropically distilled from 2.0 g of $FeCl_2 \cdot 4H_2O$ suspended in 100 ml of refluxing benzene under nitrogen for 24 hr. Triphenylphosphine (TPP) (5.0 g) was added and the mixture was refluxed for 6 hr. The solution was filtered hot under nitrogen and a few colorless crystals separated on cooling. The volume was then reduced to ~15 ml yielding additional product which was washed with benzene and ether under nitrogen. *Anal.* Calcd for $C_{36}H_{30}Cl_2FeP_2$: C, 66.40; H, 4.61; Cl, 10.89. Found: C, 65.92; H, 4.49; Cl, 11.02.

Dibromobis(triphenylphosphine)iron(II).—This light yellow compound was prepared by a method analogous to that of the chloride. *Anal.* Calcd for $C_{36}H_{30}Br_2FeP_2$: C, 58.43; H, 4.05; Br, 21.60. Found: C, 58.43; H, 4.05; Br, 21.36.

Diiodobis(triphenylphosphine)iron(II).—This was prepared analogously to the above compounds from hydrated iron(II) iodide prepared by dissolving iron metal in aqueous hydriodic acid, the excess water being removed under reduced pressure with heat. The azeotropic distillation of water from the benzene suspension was continued for 4 hr, and after addition of TPP an additional reflux period of 18 hr was allowed. The dark brownish black product was washed with benzene and ether under nitrogen. *Anal.* Calcd for $C_{36}H_{30}FeI_2P_2$: C, 51.84; H, 3.60; I, 30.43. Found: C, 51.82; H, 3.68; I, 30.35.

Dibromobis(tri-*p*-tolylphosphine)iron(II).—This was prepared in a manner analogous to $Fe(TPP)_2I_2$. The light yellowish product separated immediately and was washed with benzene and ether under nitrogen. *Anal.* Calcd for $C_{42}H_{42}Br_2FeP_2$: C, 61.23; H, 5.10. Found: C, 61.42; H, 5.22.

Proton Magnetic Resonance Spectra.—The pmr spectra were obtained using a Varian A-60-A instrument equipped with a variable-temperature probe. The spectra were calibrated using a wide-range oscillator and frequency counter to impress side bands of the internal standard, 1% TMS, onto the spectra. Samples were weighed out under nitrogen and dissolved in freshly dried (over molecular sieves) deuteriochloroform which had been deoxygenated in the usual manner.[11] The pmr sample tubes were sealed off *in vacuo* as described elsewhere.[11]

Electronic Spectrum.—The visible and near-infrared spectrum of $Fe(TPP)_2Br_2$ measured in chloroform solution in 1-cm cells on a Cary 14 instrument showed a broad band at 6410 cm^{-1} with ϵ_{max} 46 l. cm/mole. There were no other features except strong charge-transfer absorption in the ultraviolet region tailing into the visible region.

Magnetic Measurements.—The powder magnetic susceptibility of $Fe(TPP)_2Br_2$ was measured by the Gouy method at 24° using a diamagnetic correction of 418×10^{-6} cgs unit[3] yielding $\chi_M^{cor} = 11,530 \times 10^{-6}$ cgs unit and $\mu_{eff} = 5.25$ BM.

Results and Discussion

The pseudo-tetrahedral coordination of iron(II) in the bromide complex is supported by the measured magnetic moment which indicates a spin-free configuration and is in the range expected and generally found[14,15] for tetrahedrally coordinated iron(II). Further support for this structure comes from the "d–d" band at 6410 cm^{-1} which, considering the relatively high position of phosphine ligands in the spectrochemical series,[4] is expected in this region by comparison with the spectra[16] of a number of tetrahedrally coordinated iron(II) complexes with significant low-symmetry distortion.

Pmr Spectra.—Owing to the relative instability of the chloride and the insolubility of the iodide in suitable solvents, we have confined our magnetic resonance studies to the triphenylphosphine (TPP) and tri-*p*-tolylphosphine (TTP) complexes of iron(II) bromide. Unlike $Ni(TAP)_2Br_2$ and $Co(TAP)_2Br_2$ which show separate resonances for coordinated and uncoordinated ligand when both are present in chloroform solution at room temperature, complete averaging of the proton resonances of coordinated and uncoordinated TAP occurs for $Fe(TAP)_2Br_2$ at room temperature. Only at *ca.* $-50°$ are separate resonances observable.

(1) This research was supported by the National Science Foundation through Grant GP6321 and by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF 49(638)-1492.

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