$(C_6H_5)_3P$,[4] in which case a pure product might be obtained if a different supporting electrolyte were used. Recent publications[5] on low-valent rhodium and iridium compounds reveal that in complexes of the above type hydrido species can be formed by abstracting a hydrogen atom from the coordinated ligand or applied solvent. The presence of a rhodium–hydrogen complex in our compounds, however, has been ruled out by ir analysis and by the reaction with phenol, which should lead to the formation of hydrogen.[5d]

Since Rh(0) has a d^9 electronic configuration, its complexes should be paramagnetic. Magnetic susceptibility measurements, however, showed that $Rh((C_6H_5)_3P)_4$ is essentially diamagnetic while $Rh((C_6H_5)_2PCH_3)_4$ is paramagnetic with a magnetic moment (1.16 BM) much less than that expected for one unpaired electron. These results can be understood by considering a metal–metal interaction similar to that found in $[Co(CO)_4]_2$

$$\underset{\text{diamagnetic}}{L_4Rh\text{–}RhL_4} \rightleftharpoons \underset{\text{paramagnetic}}{2L_4Rh}$$

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[4] E. W. Abel, *Chem. Commun.*, 465 (1968).

[5] (a) M. A. Bennett and D. L. Milner, *ibid.*, 581 (1967); (b) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965); (c) G. Hata, A. Miyake, and H. Kondo, *J. Am. Chem. Soc.*, **90**, 2278 (1968); (d) W. Keim, *J. Organometal. Chem.* (Amsterdam), **14**, 179 (1968); (e) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *Chem. Commun.*, 548 (1968).

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A New Example of $^5T_{2g}$–$^1A_{1g}$ Equilibrium for Iron(II)

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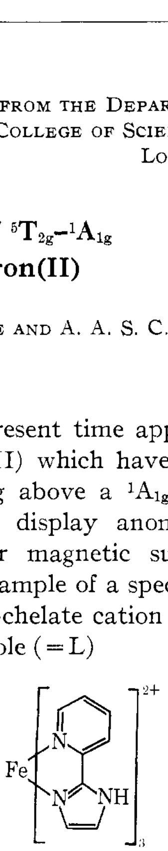
Received April 7, 1969

There is at the present time appreciable interest in compounds of iron(II) which have a thermally accessible $^5T_{2g}$ level lying above a $^1A_{1g}$ ground state[1] and which consequently display anomalous temperature dependence of their magnetic susceptibilities.[2] We report here a new example of a species having this type of behavior, the tris-chelate cation (I) of iron(II) with 2-(2′-pyridyl)imidazole (=L)



I

The formation constants for the species FeL^{2+}, FeL_2^{2+}, and FeL_3^{2+} in aqueous solution have been determined by Eilbeck and Holmes,[3] and deep red $[FeL_3](ClO_4)_2 \cdot H_2O$ was isolated by Chiswell, *et al.*,[4] who reported it as having a magnetic moment of 5.42 BM at 293°K. As part of our research program concerning the electronic properties of metal complexes with ligands containing the imidazole ring we prepared samples of this compound but found it to have a magnetic moment of only 2.50 BM at 293°K. Variable-temperature magnetic studies showed that the magnetic moments were markedly temperature dependent. (Table I lists the results for a typical run, which involved cooling the sample from room temperature to *ca.* 86°K, heating it to *ca.* 342°K, and then cooling it to room temperature again.) The susceptibility at each temperature was independent of field strength, measurements of different samples gave reproducible results, and there was no time dependence such as that observed for $Fe(phen)_2X_2$ (X = NCS or NCSe)[5] and bis(2-(2-pyridylamino)-4-(2-pyridyl)thiazole)iron(II) nitrate.[6] Moreover, results obtained cooling the sample and those obtained at increasing temperatures fell on the same curve (Figure 1). These results indicate the presence of a spin equilibrium between a $^1A_{1g}$ ground state and a thermally accessible $^5T_{2g}$ level in this compound.

Mössbauer measurements support this conclusion. At room temperature the Mössbauer spectrum consisted of a strong doublet centered at +0.63 mm/sec[7] with a quadrupole splitting (QS) of 0.37 mm/sec. There was also a weak band at *ca.* +2.24 mm/sec and a weak shoulder at *ca.* +0.25 mm/sec on the low-velocity component of the strong doublet. At 80°K the doublet had increased in intensity (with isomer shift, $\delta = 0.71$ mm/sec and QS = 0.54 mm/sec) but the weak absorptions in the +0.25- and +2.24-mm/sec regions had virtually disappeared. These results are consistent with the presence of iron atoms in $S = 0$ and $S = 2$ states with slow relaxation (this contrasts with the Mössbauer results for iron(III) dithiocarbamates where fast electronic relaxation between the spin states results in time-averaged spectra).[8]

The strong doublet centered at +0.63 mm/sec is attributed to the iron atoms in the $S = 0$ state. The QS is larger than those reported for some other low-spin tris-chelate iron(II) cations (*e.g.*, for $Fe(phen)_3^{2+}$ QS ≈ 0.16 mm/sec[9]) presumably because the unsymmetrical nature of L as a chelate induces a greater departure from O_h symmetry with a concomitant increase in the splitting of the $^5T_{2g}$ level.

The weak band in the +2- to +2.5-mm/sec region represents one component of the $S = 2$ absorption. The other component appears as the weak shoulder at

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[1] O_h notation is used here and subsequently for convenience, although it is recognized that the metal atom site symmetries in these and previously reported compounds of this type are lower than this.

[2] E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev.* (London), **22**, 457 (1968).

[3] W. J. Eilbeck and F. Holmes, *J. Chem. Soc., A*, 1777 (1967).

[4] B. Chiswell, F. Lions, and B. Morris, *Inorg. Chem.*, **3**, 110 (1964).

[5] A. T. Casey and F. Isaac, *Australian J. Chem.*, **20**, 2765 (1967).

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[7] All shifts are relative to the center of the spectrum of sodium nitroprusside at 293°K.

[8] R. M. Golding and H. J. Whitfield, *Trans. Faraday Soc.*, **62**, 1713 (1966).

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TABLE I

TEMPERATURE DEPENDENCE OF THE MAGNETIC PROPERTIES OF $[FeL_3](ClO_4)_2 \cdot H_2O$

Temp, °K	$10^6\chi_M$,[a] cgsu	μ_{eff}, BM	Procedure[b]	Temp, °K	$10^6\chi_M$,[a] cgsu	μ_{eff}, BM	Procedure[b]
341.7	4900	3.66	. .	230.5	1010	1.37	H
325.5	4280	3.35	C	216.7	730	1.16	C
311.3	3400	2.92	H	180.3	540	0.88	H
297.5	2890	2.63	C	168.5	510	0.83	C
278.5	2090	2.12	H	137.5	510	0.75	H
270.4	1960	2.07	C	119.5	480	0.62	C
257.5	1490	1.76	H	85.7	570	0.63	. .
243.9	1200	1.54	C				

[a] Corrected for diamagnetism of ligands. [b] C = cooling; H = heating.

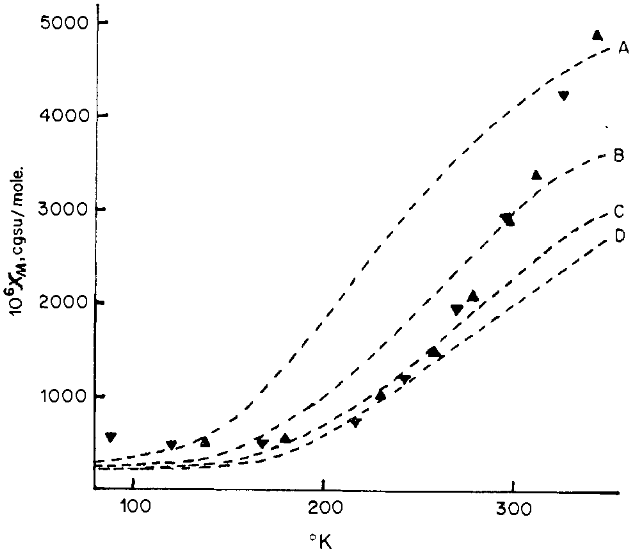

Figure 1.—Temperature dependence of the magnetic susceptibility: ▼, cooling; ▲, heating. The dotted lines are calculated from eq 4 of ref 10 using the values: (A) $\lambda = -80$ cm^{-1}, $\Delta E = 800$ cm^{-1}; (B) $\lambda = -80$ cm^{-1}, $\Delta E = 900$ cm^{-1}; (C) $\lambda = -70$ cm^{-1}, $\Delta E = 950$ cm^{-1}; (D) $\lambda = -80$ cm^{-1}, $\Delta E = 1000$ cm^{-1}, and $N\alpha = 200 \times 10^{-6}$ cgsu/mol.

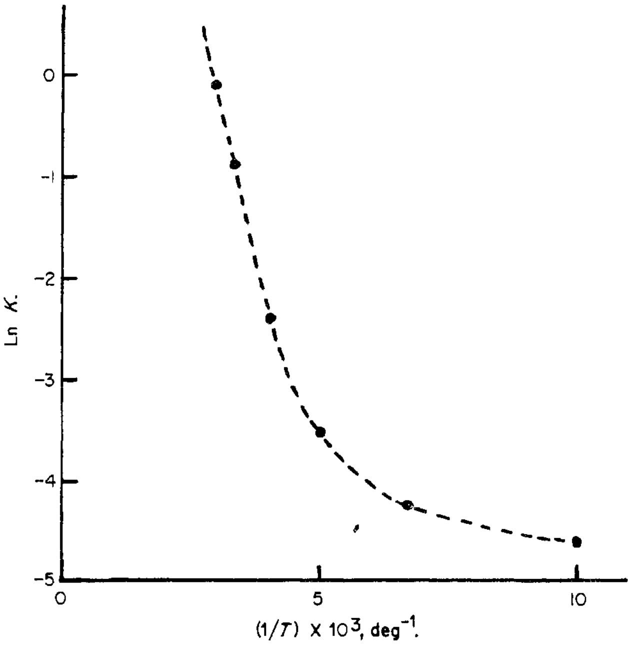

Figure 2.—Plot of ln K against $1/T$.

ca. +0.25 mm/sec and is virtually hidden by the very strong $S = 0$ absorption. Consequently, we can give only very approximate Mössbauer parameters of $\delta \approx +1.25$, and QS ≈ 2.0 mm/sec, but these are comparable with those of other high-spin distorted octahedral iron(II) systems.

Two approaches have been employed previously to interpret quantitatively the temperature dependence of the magnetic moments of systems displaying spin quintet–singlet equilibria. The first involves the calculation of the temperature dependence of the susceptibility in terms of a Boltzmann distribution between the levels arising from the two states which are separated by a fixed energy gap ΔE (cm^{-1}).[10] This approach is not successful in the present case (a representative selection of calculated curves is given as dotted lines in Figure 1), and others have reported a similar inadequacy in related systems.[6,10]

The second approach is an empirical one in which one calculates an equilibrium constant in terms of the relative concentrations of high- and low-spin forms.[2,6] Figure 2 shows the temperature dependence of ln K calculated from the experimental susceptibilities of $[FeL_3](ClO_4)_2 \cdot H_2O$. In these calculations it was assumed that the high-spin form would in the absence of spin-equilibrium obey the Curie–Weiss law with χ_M values of $11{,}000 \times 10^{-6}$ cgsu/mol at 300°K and $30{,}000 \times 10^{-6}$ cgsu/mol at 100°K and that the second-order Zeemann contribution to the susceptibility of the $S = 0$ species would be 200×10^{-6} cgsu/mol (these represent typical experimental values for such species).

The curvature of the ln K *vs.* $1/T$ plot reveals that this method is also inadequate over the full temperature range, although ΔH is essentially constant at 4.19 kcal/mol over the range 340–225°K, for which the ΔS value is 12.3 eu. These thermodynamic parameters are close to those found[11] for bis(tris(1-pyrazolyl)borate)iron(II) over a similar temperature range. The entropy term for a simple spin equilibrium between singlet and quintet levels would be only 3.2 eu, so it appears that additional factors such as bond length and angle changes play an important part in deciding the precise nature of the temperature variations of the magnetic susceptibilities.

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[10] See, for example, E. König and K. Madeja, *Inorg. Chem.*, **6**, 48 (1967).

[11] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3158 (1967).

Experimental Section

Preparations.—Both the ligand and the complex were prepared following the procedures of Chiswell, *et al.*[4]

The preparations of the complex were performed under N_2 and all of the solvents were deoxygenated by bubbling N_2 through them. In a typical preparation, a solution of 2.2 g of the ligand in 10 ml of ethanol was added to a solution of 1.8 g of iron(II) perchlorate hexahydrate in 10 ml of water. The dark red solution was concentrated to half-volume by warming and passing N_2 through. The complex precipitated on cooling and scratching. It was recrystallized from 1:1 ethanol–water (20 ml), dark red crystals being obtained. These were washed with ether and dried under vacuum (over P_2O_5) for 24 hr (68% yield). *Anal.* Calcd for $C_{24}H_{23}Cl_2FeN_9O_9$: C, 40.7; H, 3.3; Fe, 7.9; N, 17.8. Found: C, 40.9; H, 3.3; Fe, 7.9; N, 17.4.

Magnetic Measurements.—These were carried out over the range 80–350°K, at field strengths of 5.0, 5.4, and 5.9 kOe, using powdered samples and the Gouy balance previously described[12] (calibrated with $HgCo(NCS)_4$). The following diamagnetic contributions were used: Fe^{2+}, −13; ClO_4^-, −32; H_2O, −13; L, −84 (all 10^{-6} cgsu/mol).

Mössbauer Measurements.—These were made with a conventional constant-acceleration spectrometer using a Laban 400 channel analyzer and a ^{57}Co–Pd source.

Acknowledgments.—A. A. S. C. M thanks the Calouste Gulbenkian Foundation, Lisbon, for a Research Studentship and the Laboratório de Química de Faculdade de Ciências do Porto for leave of absence. We thank the SRC for the use of the Mössbauer spectrometer at Queen Elizabeth College, London.

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Direct Photolysis and Electric Discharge Decomposition of Silane–Silane-d_4 Mixtures

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Received February 3, 1969

Disilane has been prepared from silane by the reaction

$$2SiH_4 \xrightarrow{\text{energy}} Si_2H_6 + H_2 \quad (1)$$

The energy has been supplied by heat,[1] silent electric discharge,[2] and mercury photosensitization.[3]

In this note, we report our results on the photolysis (1470 Å) and silent electric discharge decomposition of equimolar silane–silane-d_4 mixtures in an attempt to elucidate the primary decomposition modes of silane for these processes.

The decomposition of silane most likely proceeds by one of the following two routes. The first is the silyl mechanism proposed for the mercury photosensitized decomposition[3]

$$SiH_4 \longrightarrow SiH_3 + H \quad (2)$$

$$H + SiH_4 \longrightarrow SiH_3 + H_2 \quad (3)$$

$$2SiH_3 \longrightarrow Si_2H_6 \quad (4)$$

or possibly

$$SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H \quad (5)$$

Without isotope effects, the products would be Si_2H_6, H_3SiSiD_3, and Si_2D_6 in a 1:2:1 ratio and H_2, HD, and D_2 in a 1:2:1 ratio, also. The second route is the silene mechanism similar to that found for the photolysis of methane[4]

$$SiH_4 \longrightarrow SiH_2 + H_2 \quad (6)$$

$$SiH_2 + SiH_4 \longrightarrow Si_2H_6 \quad (7)$$

For this route, the products would be equal quantities of Si_2H_6, 1,1-$D_2Si_2H_4$, 1,1-$H_2Si_2D_4$, and Si_2D_6 and also equal quantities of H_2 and D_2.

The results from the photolysis of equimolar mixtures of SiH_4 and SiD_4 are listed in Table I. The low quantity of HD and lack of $Si_2H_3D_3$ argue against the silyl mechanism. The lack of $Si_2H_3D_3$ also implies that H atoms were not present (from any other process) since they would produce silyl radicals from the hydrogen abstraction of silane.

We propose that the main primary process is molecular hydrogen elimination (eq 6). The energy at 1470 Å is equal to 195 kcal/mol and therefore the silenes produced would be hot. Thus the disilanes formed from silene insertion would be hot by about 155 kcal/mol. Our results on the pyrolysis of disilane[5] are in accord with decomposition into silene and silane. If the hot disilanes (Si_2D_6, 1,1-$H_2Si_2D_4$, 1,1-$D_2Si_2H_4$, and Si_2H_6) decompose into silanes and silenes, the silenes formed would be SiD_2, SiH_2, and HSiD. The insertion of HSiD into SiH_4 and SiD_4 would explain the presence of DSi_2H_5 and HSi_2D_5. The mixed silanes formed from the decomposition of the hot disilanes would also be hot, by about 82 kcal/mol, and would decompose into silenes, H_2, HD, and D_2.

The 1470-Å photolysis of methylsilane has been recently examined.[6] The results of this study are in agreement with the formation of silene, methylsilene, and possibly CH_2SiH_2.

The results from the silent electric discharge decomposition of equimolar SiH_4–SiD_4 mixtures are listed in Table II. It is apparent that the reaction is pressure dependent. This could be due to collisional deactivation at higher pressure and/or higher energies at lower pressures. The energy of the exciting electrons is a function of the distance traveled before encountering a molecule. For the high-pressure runs, the decrease in the relative concentration of D_5Si_2H, D_3SiSiH_3, and HD demonstrates that they are products of secondary reactions. Therefore, our results are in accord with the formation of disilanes from the insertion of silene into silane. It should be pointed out that our disilane analyses are most accurate for the more highly deuterated disilanes since at higher m/e values (68, 67, 66, 65) only a few molecules contribute intensities.

Our results also favor the main primary decomposi-

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