transition would also account for the enhanced Raman intensity of the 531-cm^{-1} mode, for which the major contribution is from Fe-C$_A$ stretching.

Relatively far below resonance, at 6328 Å, the depolarization ratio of the 284-cm^{-1} mode is appreciably less than $^1/_3$. This means that one of the elements α'_{xx} or α'_{yy} must have the same sign as α'_{zz} (see eq 1) and consequently, in view of the above analyses, that α'_{xx} and α'_{yy} must differ in sign.

Registry No. $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$, 40269-58-7.

Acknowledgment. We are indebted to Professor Rowland Pettit and Dr. Kenny Nicholas for providing the sample of $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$, and to Dr. Llewellyn Jones for help with the normal-coordinate analyses.

Contribution from the Istituto di Chimica Generale e Inorganica
dell'Universita di Firenze e Laboratorio CNR, 50132 Florence, Italy

Iron(II), Cobalt(II), and Nickel(II) Complexes with the Open-Chain, Tetradentate Ligand Hexaphenyl-1,4,7,10-tetraphosphadecane. Singlet Ground-State Five-Coordinated Iron(II) Complexes

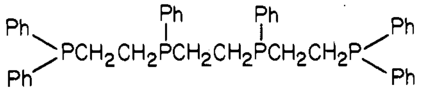
M. BACCI, S. MIDOLLINI, P. STOPPIONI, and L. SACCONI*

Received December 4, 1972

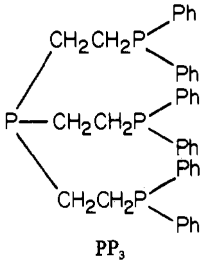
Several five-coordinate metal(II) complexes with the open-chain tetradentate ligand hexaphenyl-1,4,7,10-tetraphosphadecane (P$_4$) having the general formula [MLX]BPh$_4$ (M = Fe, Co, Ni; X = Cl, Br, I) were prepared and characterized. Spectral and X-ray information suggest a square-pyramidal geometry for all the complexes. The cobalt(II) and nickel(II) complexes are low spin. The magnetic properties of the iron(II) complexes are consistent with a spin equilibrium between a singlet ground state and a thermally accessible low-lying triplet state. For purposes of comparison we also prepared the [Fe(PP$_3$)Br]BPh$_4$ complex, where PP$_3$ is the ligand tris(2-diphenylphosphinoethyl)phosphine. The thiocyanate complexes Fe(L)(NCS)$_2$ (L = P$_4$, PP$_3$) are diamagnetic and probably have a pseudooctahedral geometry.

Introduction

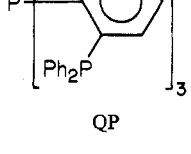
Phosphorus is the most nucleophilic donor atom known and thus five-coordinate metal complexes containing it as donor atom have ground states of the lowest possible spin multiplicity.[1] Excluding the set P$_5$ the most nucleophilic sets are of the type P$_4$X (X = halogen or pseudohalogen) which in general involve phosphorated tetradentate ligands. The ligands of this type which have been used to date are tris(*o*-diphenylphosphinophenyl)phosphine (QP),[2] tris(2-diphenylphosphinoethyl)phosphine (PP$_3$),[3] both of which have a tripod structure, and the open-chain ligand hexaphenyl-1,4,7,10-tetraphosphadecane (P$_4$) (I).[3] With bivalent 3d metal ions these ligands give five-coordinate complexes [M(P$_4$)X]$^+$; the cobalt(II) and nickel(II) complexes are all low-spin. So far iron(II) complexes have only been prepared with the first two ligands. They are found to have approximately trigonal-bipyramidal geometry and a triplet ground state. All other known five-coordinate complexes of iron(II) have less than four phosphorus atoms in the donor set and either have a quintuplet ground state[4] or are involved in a $^5E \rightleftharpoons {}^3A$ equilibrium.[5] On the other hand on the basis of theoretical considerations it appears that, if it is possible for a five-coordinate iron(II) complex to exist in a singlet ground state, this will occur when the geometry is approximately square pyramidal (C_{4v} symmetry or less) and when the donor atom set has a maximum overall nucleophilicity.



P$_4$



PP$_3$



QP

Since it seemed probable that with the open-chain ligand P$_4$ five-coordinate complexes having a square-pyramidal structure would be obtained, we decided to see if we could prepare five-coordinate iron(II) complexes with this ligand. We now report that, in spite of previous failures to prepare them, five-coordinate iron(II) complexes can be prepared with the ligand P$_4$. They have the general formula [Fe(P$_4$)X]BPh$_4$ (X = halogen) and in some cases crystallize with CH$_2$Cl$_2$ of crystallization. The analogous complexes of cobalt(II) and nickel(II) were also prepared.

All the complexes were characterized and their physical properties studied by the usual methods.

Previously only four-coordinated square-planar complexes of nickel(II) with ligand P$_4$ were reported.[3]

Experimental Section

The ligands P$_4$ and PP$_3$ were obtained from the Pressure Chemical Co. All the solvents used were reagent grade. The iron(II) complexes were all prepared and stored under nitrogen.

Preparation of the Complexes Fe(P$_4$)X(BPh$_4$), X = Cl, Br, I. A solution of anhydrous FeX$_2$ (1 mmol) in absolute ethanol was added to a solution of the ligand (1 mmol) in methylene chloride (20 ml).

---

(1) L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

(2) L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 3, 453 (1964); B. T. Halfpenny, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 627 (1967).

(3) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, 10, 1851 (1971).

(4) L. Sacconi, *Pure Appl. Chem.*, 27, 161 (1971).

(5) W. S. J. Kelly, G. H. Ford, and S. M. Nelson, *J. Chem. Soc. A*, 388 (1971); W. U. Dahlhoff and S. M. Nelson, *ibid.*, 2184 (1971).

After 1 mmol of sodium tetraphenylborate dissolved in absolute ethanol had been added to this solution, the methylene chloride was removed by bubbling nitrogen through the unheated solution. The crystals which formed were filtered, washed with ethanol and then with petroleum ether, and finally dried in a current of nitrogen. They were recrystallized from methylene chloride and absolute ethanol.

$FeL(NCS)_2$, L = P_4, PP_3. Potassium thiocyanate (2 mmol) dissolved in absolute ethanol (30 ml) was added to the solution obtained by mixing 1 mmol of $FeCl_2$ dissolved in ethanol (30 ml) with 1 mmol of ligand dissolved in methylene chloride (20 ml). After removal of the methylene chloride by passing a current of nitrogen through the solution, crystals formed and they were separated and recrystallized from methylene chloride and absolute alcohol.

$Fe(PP_3)Br(BPh_4)$. This compound was prepared by the method used[3] to prepare the analogous complex $Fe(PP_3)Cl(PF_6)$.

$M(P_4)X(BPh_4)$, M = Ni, Co and X = Cl, Br, I, NCS. All these compounds were prepared by the methods described above for the analogous iron(II) complexes.

Physical Measurements. Magnetic susceptibilities were measured using the Gouy method, the apparatus and experimental technique being those previously described.[6] The Gouy tube was calibrated using distilled water and $Hg[Co(NCS)_4]$.[7] Diamagnetic corrections were calculated using Pascal's constants.[7] The electronic and ir spectra, the molar conductivities, the molecular weights, and the X-ray powder patterns were all obtained using the methods described elsewhere.[8]

Results

The analytical data together with some of the physical data are shown in Table I. All the complexes are soluble in chloroform, methylene chloride, and 1,2-dichloroethane and the iron(II) thiocyanate complex is also soluble in benzene. The iron(II) complexes in the solid state are not oxidized appreciably by dry air but in solution they slowly decompose even in anhydrous solvents.

The conductivity data (Table I) found for the compounds $M(P_4)X(BPh_4)$ are typical of those found for 1:1 electrolytes under the same conditions.[9] The complex $Fe(P_4)(NCS)_2$ is found to be essentially a nonelectrolyte and molecular weight measurements in the same solvent show it to be monomeric (Table I).

The results of the magnetic susceptibility measurements carried out at room temperature on powder samples of the complexes are also shown in Table I. The cobalt(II) and nickel(II) complexes are all low spin while among the iron(II) complexes the thiocyanate, $Fe(P_4)(NCS)_2$, is diamagnetic and the compounds $Fe(P_4)Cl(BPh_4)\cdot 1.5CH_2Cl_2$, $Fe(P_4)Br(BPh_4)\cdot CH_2Cl_2$, and $Fe(P_4)I(BPh_4)$ have magnetic moments whose values lie between those expected for $S = 0$ and $S = 1$. The magnetic behavior of the last three compounds has been studied in detail over the range 84-380°K (Table II); it was not possible to go above 380°K because of decomposition. Figure 1 shows χ_M^{-1} and μ_{eff} plotted against temperature between 84 and 380°K for the bromo complex. None of the three complexes obeys the Curie-Weiss law and in no case is the susceptibility found to be field dependent.

The diffuse reflectance spectra of the complexes are in all cases similar to those found in 1,2-dichloroethane solution (Table III, Figure 2). The small shifts in the frequencies of the absorption maxima, which are found for the complexes of all three metals as the halogen is changed, can be attributed to the normal spectrochemical shift. The reflectance spectra of the iron(II) complexes were measured both at room temperature and at *ca.* 160°K.

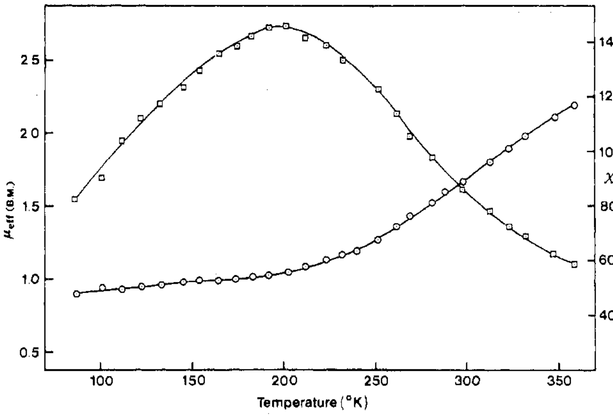


Figure 1. Variation of the magnetic moment μ_{eff} (○) and the inverse of corrected molar susceptibility χ_M^{-1} (□) with temperature for $[Fe(P_4)Br]BPh_4\cdot CH_2Cl_2$.

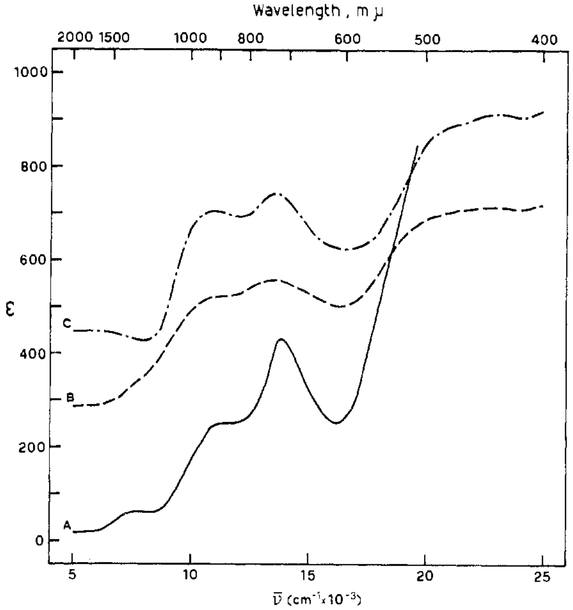


Figure 2. Absorption spectrum of $[Fe(P_4)I]BPh_4$ in 1,2-dichloroethane (curve A). Solid-state spectra (arbitrary scale) of $[Fe(P_4)I]BPh_4$ at 25° (curve B) and at −160° (curve C).

The X-ray powder patterns of the complexes $M(P_4)X(BPh_4)$, where M = Fe, X = I; M = Co, X = Br, I; and M = Ni, X = Br, I, are practically identical.

Discussion

The molar conductivities of the cobalt(II) and nickel(II) complexes clearly show them to be 1:1 electrolytes of general formula $[M(P_4)X]BPh_4$. The essentially identical electronic spectra obtained from the solids and from the 1,2-dichloroethane solutions for all the complexes show that the stereochemistry is the same in both states. Both the appearance of the spectra and the values of the magnetic moments are characteristic of five-coordinate low-spin complexes. The electronic spectra of the nickel(II) complexes have two bands at *ca.* 17,000-20,000 and 21,800-25,000 cm^{-1} which can be assigned, in terms of the spin-allowed transitions in C_{4v} symmetry,[10] as $^1A_1 \rightarrow {}^1B_1$ and $^1A_1 \rightarrow {}^1E$ of which only the latter is orbitally allowed. The third band expected in C_{4v} symmetry, $^1A_1 \rightarrow {}^1A_2$, is generally masked by a charge-transfer band. On the other hand the relative

---

(6) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Amer. Chem. Soc.*, 82, 3487 (1960).

(7) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 400.

(8) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 7, 1417 (1968).

(9) W. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971).

(10) J. R. Preer and H. B. Gray, *J. Amer. Chem. Soc.*, 92, 7306 (1970).

Table I. Physical Constants and Analytical Data

Compd	Color	Λ_M,[a] cm^2 ohm^{-1} mol^{-1}	Anal., % Calcd C	Calcd H	Calcd M	Found C	Found H	Found M	μ_{eff}, BM (298°K)
$[Fe(P_4)Cl]BPh_4\cdot 1.5CH_2Cl_2$ [b]	Emerald green	24	69.0	5.5	4.8	69.7	5.6	4.8	1.35
$[Fe(P_4)Br]BPh_4\cdot CH_2Cl_2$ [c]	Emerald green	22	64.7	5.3	4.5	65.9	5.9	4.4	1.67
$[Fe(P_4)I]BPh_4$ [d]	Brown	23	67.5	5.0	4.9	67.4	5.3	4.9	1.60
$[Fe(P_4)(NCS)_2]$ [e]	Chedron		62.8	5.0	6.5	62.0	4.7	6.5	Diam
$[Co(P_4)Cl]BPh_4$ [f]	Brown sugar	22	73.1	5.8	5.4	72.5	5.8	5.4	1.98
$[Co(P_4)Br]BPh_4$	Brown	23	70.2	5.5	5.2	70.5	6.0	5.0	1.98
$[Co(P_4)I]BPh_4$ [g]	Tobacco	21	67.4	5.3	5.0	67.4	5.5	5.0	2.13
$[Co(P_4)(NCS)]BPh_4$ [h]	Brown	24	71.7	5.7	5.3	72.0	5.6	5.3	2.04
$[Ni(P_4)Cl]BPh_4$	Brown	26	73.1	5.8	5.4	74.0	6.0	5.3	Diam
$[Ni(P_4)Br]BPh_4$	Brick red	24	70.2	5.5	5.2	70.2	5.5	5.6	Diam
$[Ni(P_4)I]BPh_4$ [i]	Dark brown	25	67.4	5.3	5.0	67.3	5.4	5.0	Diam
$[Ni(P_4)(NCS)]BPh_4$ [j]	Red-brown	19	72.7	5.7	5.3	72.8	5.9	6.0	Diam
$[Fe(PP_3)Br]BPh_4$	Purple	19	70.4	5.5	5.0	69.3	5.8	4.8	3.02
$[Fe(PP_3)(NCS)_2]$ [k]	Chedron		62.8	5.8	4.9	61.3	5.0	5.8	Diam

[a] Molar conductance values for 10^{-3} *M* 1,2-dichloroethane solutions. [b] Calcd: Cl, 9.1. Found: Cl, 10.2. [c] Calcd: P, 9.8. Found: P, 9.8. [d] Calcd: P, 10.6. Found: P, 10.5. [e] Calcd: N, 3.3; mol wt 842. Found: N, 2.8; mol wt 829. [f] Calcd: Cl, 3.2. Found: Cl, 3.1. [g] Calcd: I, 10.8. Found: I, 10.5. [h] Calcd: N, 1.3. Found: N, 1.3. [i] Calcd: I, 10.8. Found: I, 10.5. [j] Calcd: N, 1.3. Found: N, 1.4. [k] Calcd: N, 3.3; mol wt 842. Found: N, 3.3; mol wt 820.

Table II. Magnetic Data for the $[Fe(P_4)X]BPh_4$ Complexes

$[Fe(P_4)Cl]BPh_4\cdot 1.5CH_2Cl_2$			$[Fe(P_4)Br]BPh_4\cdot CH_2Cl_2$			$[Fe(P_4)I]BPh_4$		
T, °K	$10^6\chi_M$, cgsu	μ_{eff}, BM	*T*, °K	$10^6\chi_M$, cgsu	μ_{eff}, BM	*T*, °K	$10^6\chi_M$, cgsu	μ_{eff}, BM
376	1281	1.97	369	1735	2.26	376.5	1528	2.16
366	1220	1.90	358	1678	2.19	366.5	1442	2.06
354	1124	1.79	347.5	1596	2.11	357.5	1381	1.99
345	1066	1.72	332.5	1459	1.97	348	1293	1.91
333	975	1.62	331	1453	1.96	336.5	1216	1.82
321	878	1.51	322.5	1384	1.89	325	1158	1.74
311	800	1.42	312	1283	1.79	316	1100	1.67
299	781	1.37	287	1120	1.60	299	1046	1.60
278	600	1.16	280.5	1032	1.52	270	931	1.43
270	560	1.10	268.5	945	1.43	260	896	1.37
260	515	1.04	261	882	1.36	250	872	1.33
250	479	0.98	251	807	1.27	240	861	1.29
239	440	0.92	239.5	744	1.19	229.5	864	1.26
228	442	0.88	231.5	750	1.17	219.5	863	1.24
218	395	0.83	223	717	1.13	210	875	1.22
208	386	0.80	211.5	705	1.09	199	891	1.20
197	376	0.77	202.5	683	1.05	187.5	918	1.18
187	337	0.75	191.5	688	1.03	176	968	1.16
177	368	0.73	183	699	1.02	168	967	1.15
168	377	0.72	173.5	724	1.00	157.5	1033	1.14
158.5	388	0.70	164	735	0.98	147	1068	1.13
148	398	0.69	153.5	771	0.98	135	1154	1.12
137.5	414	0.68	145	812	0.97	125	1211	1.10
127.5	432	0.67	132.5	852	0.99	115	1290	1.09
118.5	456	0.66	122	920	0.95	106.5	1372	1.09
108.5	474	0.64	111.5	958	0.93	97.5	1519	1.09
99.5	510	0.64	100.5	1108	0.94			
86	591	0.64	86	1208	0.89			

Table III. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

Compd		Absorption max,[a] cm^{-1} (ϵ_M for soln)
$[Fe(P_4)Cl]BPh_4\cdot 1.5CH_2Cl_2$	a:	8400 sh, 11,980 sh, 15,150, 23,000
	a′:	11,980, 15,150
	b:	8065 (42), 12,195 (300), 15,150 (596)
$[Fe(P_4)Br]BPh_4\cdot CH_2Cl_2$	a:	8450 sh, 11,780 sh, 15,000, 23,000
	a′:	11,780, 15,000, 23,000
	b:	8000 (44), 11,830 (234), 14,920 (450), 24,390 (1400)
$[Fe(P_4)I]BPh_4$	a:	7600 sh, 11,100 sh, 13,600, 22,000 sh
	a′:	11,100, 13,600, 21,400, 23,600
	b:	7575 (63), 11,360 (253), 13,985 (433)
$[Fe(P_4)(NCS)_2]$	a:	20,000, 23,810
	b:	19,230 (520), 23,810 (1260), 27,780 (1790)
$[Co(P_4)Cl]BPh_4$	a:	8330, 10,500, 14,000, 18,200 sh, 22,100 sh, 25,600
	b:	8270 (140), 10,520 (83), 13,520 (223), 18,190 (521), 22,280 sh, 25,680 sh
$[Co(P_4)Br]BPh_4$	a:	8060, 10,000, 13,340, 18,200 sh, 22,230 sh, 26,350 sh
	b:	8000 (125), 10,000 (77), 13,180 (183), 17,850 (500), 22,200 sh, 25,330 sh
$[Co(P_4)I]BPh_4$	a:	7940, 9800, 12,900, 17,600 sh, 22,200 sh
	b:	7940 (158), 9700 (92), 12,900 (230), 17,700 (500), 21,300 (2150)
$[Co(P_4)NCS)]BPh_4$	a:	7360, 9600, 13,050, 18,890, 23,140
	b:	8000 (215), 10,030 (119), 13,300 (168), 18,500 sh, 22,800 (5600)
$[Ni(P_4)Cl]BPh_4$	a:	19,050 sh, 25,530
	b:	18,900 sh (350), 25,000 (1870)
$[Ni(P_4)Br]BPh_4$	a:	20,410 sh, 25,000
	b:	19,200 sh (356), 25,000 (1461)
$[Ni(P_4)I]BPh_4$	a:	17,390 sh, 21,750
	b:	21,000 sh (890), 24,390 (1550)
$[Ni(P_4)NCS]BPh_4$	a:	19,050 sh, 23,530
	b:	18,200 sh (692), 23,000 (2260)
$[Fe(PP_3)Br]BPh_4$	a:	8000, 18,870
	b:	8330 (520), 18870 (3170)
$[Fe(PP_3)(NCS)_2]$	a:	21,000, 28,000 sh
	b:	21,000 (1790)

[a] Key: a, solid at room temperature; a′, solid at *ca.* 160°K; b, 1,2-dichloroethane solution.

intensities of the two bands predicted in D_{3h} symmetry, $^1A_1 \rightarrow {}^1E'$ and $^1A_1 \rightarrow {}^1E''$, would be the opposite of those found experimentally in the present case.[1,11]

The electronic spectra of the cobalt(II) complexes are such that it is not possible to distinguish between the two limiting geometries. However the isomorphism of the iodo and bromo complexes with the corresponding nickel(II) compounds shows that they too must have an approximately square-pyramidal geometry.

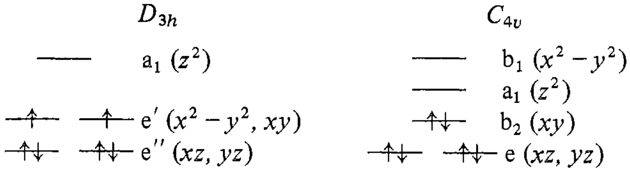
The electronic spectrum of the complex $Fe(P_4)(NCS)_2$ closely parallels those of $Fe(QP)(NCS)_2$, to which an octahedral structure has been assigned,[2] and of $Fe(PP_3)(NCS)_2$, which we prepared specifically for purposes of comparison. However the ir spectra of the complexes $Fe(P_4)(NCS)_2$ and $Fe(PP_3)(NCS)_2$ show respectively a single band at 2115 cm^{-1} and two bands at 2100 and 2120 cm^{-1} in the (CN) stretching region. It therefore seems reasonable to assign a trans octahedral structure to the P_4 complex and a cis octahedral structure to the PP_3 complex.

The electronic spectra of the three iron(II) complexes

(11) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **90**, 5443 (1968).

$[Fe(P_4)X]BPh_4$ are very similar to each other, and since $[Fe(P_4)I]BPh_4$ is isomorphous with the analogous cobalt(II) and nickel(II) compounds, it would seem reasonable to assign a square-pyramidal geometry to all three iron(II) compounds. As will be seen below it is difficult to explain the magnetic data unless we assume they have this geometry.

The simple crystal field model for a five-coordinate d^6 ion in a strong field shows that a singlet ground state is not possible in D_{3h} symmetry and only a greater or lesser distortion in the direction of a square-pyramidal structure can stabilize such a ground state (it is well known that it is possible to go from a D_{3h} structure to a C_{4v} structure *via* a C_{2v} structure[12]).



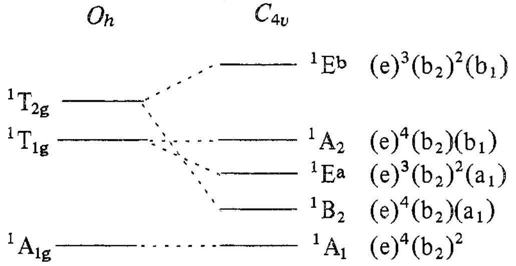
II

The magnetic data do in fact show that the $[Fe(P_4)X]BPh_4$ complexes are essentially in a singlet ground state at liquid nitrogen temperature (Figure 1), the limiting μ_{eff} value of <1.0 BM at 86°K being attributed to TIP. The complex $[Fe(PP_3)Br]BPh_4$ has an electronic spectrum very similar to those of the trigonal-bipyramidal complexes $[Fe(QP)X]BPh_4$ and a μ_{eff} of 3.03 BM and obeys the Curie-Weiss law with $\Theta = 0°$.

In view of the fact that the Fe(II)-iodo complex is isostructural with the analogous cobalt(II) and nickel(II) complexes, both of which show normal magnetic behavior, it is not possible to attribute the variation of μ_{eff} with temperature to antiferromagnetic interactions. Even above room temperature the values of μ_{eff} remain lower than those expected for an $S = 1$ system but the steady upward trend does suggest that there must be a spin equilibrium between a singlet ground state and a thermally accessible triplet state. We consider that these compounds, unlike many others for which a spin equilibrium with inversion of the ground state spin multiplicity has been postulated,[13] always have a singlet ground state; this accounts for the rather low μ_{eff} values which are found even at high temperature. In fact it is a gross oversimplification to talk about pure singlet and triplet states in the neighborhood of a crossover point. In this region pure spin states do not exist, states of different spin multiplicity being mixed *via* spin-orbit coupling.

The recent theoretical work by Konig, *et al.*,[14] has shown that the best fit of the experimental and calculated values is obtained by assuming that ϵ, the difference in energy between the two states of different spin multiplicity, is a function of temperature. If we look at the schematic energy level diagram (II) it seems reasonable to suppose that in the case of our compounds the energy gap between the states a_1 and b_2 must decrease with increasing temperature, possible through an increase in the Fe-apical donor atom distance. A recent X-ray study of the complex $Fe(dipy)_2(NCS)_2$ at various temperatures showed that there are considerable differences in the bond lengths and bond angles in the two forms of different spin multiplicity.[15]

The electronic spectra of the complexes $[Fe(P_4)X]BPh_4$ (Figure 2), which are very different from the spectra of the trigonal-bipyramidal complexes of iron(II) reported in the literature,[2,3] have a band at 7500-8500 cm^{-1} which is very temperature dependent. We can assign this band to a singlet-triplet transition. The increase of intensity with temperature can then be accounted for by an increased mixing-in of the triplet state into the ground state. At liquid nitrogen temperatures the complexes can be considered for all practical purposes to have a singlet ground state and the electronic spectra can be tentatively interpreted by supposing the $[Fe(P_4)X]^+$ chromophore to have C_{4v} symmetry with the four phosphorus atoms in the equatorial plane. The latter assumption seems to be justified by the ligand geometry as shown by the trans octahedral structure of the complex $Fe(P_4)(NCS)_2$. The order of the energy levels for a five-coordinate d^6 ion in C_{4v} symmetry (strong field) can be assumed to be as shown in III.



III

On this basis we can assign the first two spin-allowed bands which occur in the low-frequency region to the transitions $^1A_1 \rightarrow {}^1B_2$ (ν_1) and $^1A_1 \rightarrow {}^1E^a$ (ν_2), of which only the second is orbitally allowed. Of the three $[Fe(P_4)X]BPh_4$ complexes only the iodide has a spectrum with two high-frequency bands which can be assigned to the transition $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E^b$. In the spectra of the other two halides there is only one band in this region and it seems probable that the other transition is obscured by a charge-transfer band. The transition energies for a d^6 ion in a strong field can be found to first order from the expressions[16]

$$E(^1B_2) - E(^1A_1) = 10Dq - 4Ds - 5Dt + 16B - C$$
$$E(^1E^a) - E(^1A_1) = 10Dq - {}^{35}/_4Dt - C$$
$$E(^1A_2) - E(^1A_1) = 10Dq - C$$
$$E(^1E^b) - E(^1A_1) = 10Dq + 2Ds - {}^{25}/_4Dt + 16B - C$$

By assuming a value of 3300 cm^{-1} for C it is possible to find approximate values for the other parameters from the energies of the four bands observed in the spectrum of the iodide complex. The choice of the value of 3300 cm^{-1} for C is made because this parameter has been found to vary about that value for other iron(II) complexes.[17] The values found for the other parameters are $Dq = 2470$ cm^{-1}, $Dt = 890$ cm^{-1}, $Ds = 2275$ cm^{-1}, and $B = 200$ cm^{-1}. Substituting these values into the expressions for the lowest energy singlet and triplet states calculated by Konig[18]

$$E(^1A_1) = -24Dq + 14Dt + 5B + 8C$$
$$E(^3A_2) = -14Dq + 14Dt + 5B + 5C$$
$$E(^3E(^3T_1)) = -14Dq + Ds + {}^{13}/_2Dt - 9B + 5C - R_1$$
$$E(^3B_2) = -14Dq - 4Ds + 9Dt + 13B + 5C$$

---

[12] M. Ciampolini, *Struct. Bonding (Berlin)*, 6, 52 (1969).

[13] E. Konig, *Coord. Chem. Rev.*, 3, 471 (1968), and references therein.

[14] E. Konig and S. Kremer, *Theoret. Chim. Acta*, 20, 143 (1971); 22, 45 (1971).

[15] E. Konig and W. J. Watson, *Chem. Phys. Lett.*, 6, 457 (1970).

[16] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4, 709 (1965).

[17] J. C. Dabrowiak, P. H. Herrell, and D. H. Busch, *Inorg. Chem.*, 11, 1979 (1972).

[18] E. Konig and R. Schnakig, *Inorg. Chim. Acta*, in press.

$$E(^3\mathrm{E}(^3\mathrm{T}_2)) = -14Dq + Ds + {}^{13}/_2Dt + 9B + 5C + R_1$$

where

$$R_1 = {}^1/_2[(2Ds + {}^{10}/_4Dt + 8B)^2 + {}^3/_4(4Ds + 5Dt)^2]^{1/2}$$

we find that there is a triplet state $^3\mathrm{E}(^3\mathrm{T}_1)$ *ca.* 400 cm^{-1} above the $^1\mathrm{A}_1$ ground state. Clearly the triplet state is thermally accessible from the ground state and this is sufficient to account for the magnetic behavior of the $[\mathrm{Fe(P_4)X}]\mathrm{BPh_4}$ complexes, even though a more accurate treatment must await the data made available by the structure determination which is in progress in these laboratories.

Registry No. $[\mathrm{Fe(P_4)Cl}]\mathrm{BPh_4}$, 39831-90-8; $[\mathrm{Fe(P_4)Br}]\mathrm{BPh_4}$, 39708-45-7; $[\mathrm{Fe(P_4)I}]\mathrm{BPh_4}$, 39708-46-8; $[\mathrm{Fe(P_4)(NCS)_2}]$, 39836-70-9; $[\mathrm{Co(P_4)Cl}]\mathrm{BPh_4}$, 39971-67-0; $[\mathrm{Co(P_4)Br}]\mathrm{BPh_4}$, 39708-47-9; $[\mathrm{Co(P_4)I}]\mathrm{BPh_4}$, 39708-48-0; $[\mathrm{Co(P_4)(NCS)}]\mathrm{BPh_4}$, 39708-49-1; $[\mathrm{Ni(P_4)Cl}]\mathrm{BPh_4}$, 39708-50-4; $[\mathrm{Ni(P_4)Br}]\mathrm{BPh_4}$, 39831-91-9; $[\mathrm{Ni(P_4)I}]\mathrm{BPh_4}$, 39708-51-5; $[\mathrm{Ni(P_4)(NCS)}]\mathrm{BPh_4}$, 39708-52-6; $[\mathrm{Fe(PP_3)Br}]\mathrm{BPh_4}$, 39708-53-7; $[\mathrm{Fe(PP_3)(NCS)_2}]$, 39836-71-0.

Acknowledgments. Thanks are expressed to Dr. J. Gelsomini and Mr. F. Nuzzi for microanalyses and to Mr. F. Zanobini, Mr. F. Cecconi, and Mr. G. Scapacci for technical assistance.

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Absolute Configuration of Aspartic Acid Complexes. The Cobalt(III) Complex of a New Stereospecific Hexadentate Ligand Containing the Aspartic Acid Unit

J. IVAN LEGG*[1] and JOHN A. NEAL

Received June 12, 1972

A series of aspartic acid complexes and related chelates have been reported in the literature, and their absolute configurations have been assigned on the basis of circular dichroism and proton magnetic resonance. From correlations of spectral data and comparison with complexes of known absolute configuration, we believe that some of the assignments are incorrect. In support of this argument we have synthesized the aspartic acid containing ligand (*S*)-ethylenediamine-*N*,*N*-diacetic-*N'*-monosuccinic acid (EDDAMS) which is of known absolute configuration. EDDAMS exhibits stereospecificity on coordination to cobalt(III) to give a complex of known absolute configuration which has been characterized by visible, ir, pmr, and CD spectroscopy. The spectral behavior of this complex supports our predictions of absolute configurations. The unusual geometry associated with the tridentate aspartic acid chelate (*e.g.*, the presence of greater-than-five-membered rings) may account for the difficulties which have arisen in assigning absolute configurations to its complexes.

Introduction

The stereochemistry of trifunctional amino acids[2] is distinct from bifunctional amino acid chelates as illustrated in Figure 1 for chelated aspartic acid. The three rings join on a face of the octahedron at the asymmetric carbon in such a manner that the rings do not clearly define edges of an octahedron as they do for other commonly encountered tridentate chelates (*e.g.*, diethylenetriamine and iminodiacetic acid chelates), and in some of the chelates the R side chain forms part of a six- or greater-than-six-membered ring. The formation of greater-than-five-membered rings may result in ligand–metal bond angles which are greater than 90°. The presence of such chelate rings may lead to complexities in the circular dichroism spectra which would make it difficult to correlate absolute configurations on the basis of optical activity alone. It has been recently shown that changing from metal-ligand bond angles of less than 90° to angles greater than 90° profoundly affects the energies and signs of electronic states.[3] These observations are consistent with a model for optical activity suggested by Piper and Karipides.[4]

A number of reports have appeared where trifunctional amino acids may function or definitely function as tridentate ligands.[5-8] Among the most thoroughly studied of the tridentate amino acid chelates are the Co(III) complexes of aspartic acid[6-8] and a closely related hexadentate ligand con-

---

(1) National Institutes of Health Special Research Fellow, Biophysics Research Laboratory, Harvard Medical School, Boston, Mass., 1972–1973. (This is Dr. Legg's address until Sept 1, 1973.)

(2) Trifunctional amino acids are defined as those which have three potential coordinating groups (*e.g.*, aspartic acid and cysteine) as compared to bifunctional amino acids with two potential coordinating groups (the α-amine and carboxylate, *e.g.*, glycine and alanine). When not explicitly stated the *S* configuration of aspartic acid is implied.

(3) T. M. Wing and R. Eiss, *J. Amer. Chem. Soc.*, **92**, 1929 (1970).

(4) T. S. Piper and A. G. Karipides, *Inorg. Chem.*, **4**, 923 (1965); A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964); T. S. Piper and A. Karipides, *Mol. Phys.*, **5**, 475 (1962); T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961). For a recent discussion of this model see K. R. Butler and M. R. Snow, *Inorg. Chem.*, **10**, 1838 (1971); *Chem. Commun.*, 550 (1971).

(5) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1857 (1969); G. N. Schrauzer and P. A. Doemeny, *J. Amer. Chem. Soc.*, **93**, 1608 (1971); A. Kay and P. C. H. Mitchell, *J. Chem. Soc. A*, 2421 (1970); R. Candlin and M. M. Harding, *J. Chem. Soc. A*, 384 (1970); L. T. J. Delbaere and C. K. Prout, *Chem. Commun.*, 162 (1971); J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 6092 (1967); C. C. McDonald and W. D. Phillips, *ibid.*, **85**, 3736 (1963); E. W. Wilson, Jr., M. H. Kasperian, and R. B. Marting, *ibid.*, **92**, 5365 (1970); D. S. Barnes and L. D. Pettit, *Chem. Commun.*, 1000 (1970); E. R. Clarke and A. E. Martell, *J. Inorg. Nucl. Chem.*, **32**, 911 (1970).

(6) A. Y. Girgis and J. I. Legg, *J. Amer. Chem. Soc.*, **94**, 8420 (1972); J. I. Legg and J. Steele, *Inorg. Chem.*, **10**, 2177 (1971); M. S. Schneller, Thesis, Washington State University, 1971; J. I. Legg, A. L. Kilbert, Jr., and W. F. Siems III, "Progress in Coordination Chemistry," Michael Cais, Ed., Elsevier, Amsterdam, 1968, p 331; J. I. Legg and D. W. Cooke, *J. Amer. Chem. Soc.*, **89**, 6854 (1967).

(7) S. Yamada, J. Hidaka, and B. E. Douglas, *Inorg. Chem.*, **10**, 2187 (1971); L. R. Froebe, S. Yamada, J. Hidaka, and B. E. Douglas, *J. Coord. Chem.*, **1**, 183 (1971).

(8) J. Hidaka, S. Yamada, and B. E. Douglas, *J. Coord. Chem.*, in press.