Complexes of Some First-row Transition Elements with (−)-Spartein

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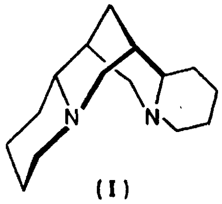
Complexes of cobalt(II), nickel(II), copper(II), and zinc(II), of the general formula [M(spartein)X_2], where X = Cl^-, Br^-, or I^-, have been prepared and characterised. Magnetic moments, electronic spectra, and the circular dichroism absorption (down to 5000 cm^{-1}) of [Ni(sp)Cl_2] are reported. The electronic structures of the cobalt(II) and nickel(II) complexes are discussed in terms of an effective C_{2v} chromophoric symmetry. Complexes of manganese(III) and iron(III) have been obtained, but are less well characterised.

THE tetracyclic tertiary diamine, (−)-spartein, with the absolute configuration,[1,2] (6*R*, 7*S*, 9*S*, 11*S*), acts as a bidentate chelating ligand in the conformation (I). Complexes of (I) with organo-lithium and magnesium derivatives [3-5] and with zinc [6] have been postulated in the asymmetric synthesis of allenes [3,4] and carbinols.[4-6] On the n.m.r. time-scale ligand-exchange in the dialkylmagnesium complexes of (I) is found to be slow.[7] The biological activity [8] of (−)-spartein has been ascribed [7] to the sequestration of magnesium, and possibly other metal ions, by (I). In the present work we report that (−)-spartein (sp) forms complexes of the type, [M(sp)X_2], X = Cl^-, Br^-, or I^-, with cobalt(II), nickel(II), copper(II), and zinc(II), which are stable in ethanol and chloroform, and complexes with iron(III) and maganese(III) which are stable only in the solid state.


(I)

RESULTS AND DISCUSSION

The analytical results (Table 1) indicate that the complexes of the divalent metal ions are formulated [M(sp)X_2], X = Cl^-, Br^-, or I^-. The stoicheiometry is analogous to that of the dialkylmagnesium complexes [7] with (I) and reflects the steric constraints upon the co-ordination of two (−)-spartein molecules to a metal ion. Iron(II) and maganese(II), under the same preparative conditions as used for the other metal ions, give complexes which analyse more satisfactorily for [M(sp)Cl_3] than [M(sp)Cl_2] (Table 1), suggesting an oxidation to the metal(III) state. The manganese complex may be polymeric, since it is insoluble in water and organic solvents. The iron complex dissolves sparingly in chloroform with some decomposition and, accordingly, the magnetic moment of the complex in this solvent, which was low and not well reproduced, is unreliable and is not reported. The presence of iron(III) in the complex is supported by the electronic spectrum which is typically that of a d^5 metal ion.

TABLE 1

Analytical results (%) [a] and magnetic moments

	C	H	N	Halogen	μ_{eff}/ B.M.
Ni(sp)Cl_2	49·3(49·6)	7·0(7·2)	7·6(7·7)	18·1(19·5)	3·69
Ni(sp)Br_2	40·0(38·9)	5·8(5·8)	6·4(6·2)	35·4(35·3)	3·66
Ni(sp)I_2	33·3(32·9)	5·0(4·8)	5·4(5·1)	45·8(46·4)	3·47
Co(sp)Cl_2	49·6(49·5)	7·2(7·2)	7·7(7·7)	17·0(19·5)	4·12 [b]
Co(sp(Br_2	39·8(39·9)	5·9(5·8)	6·4(6·2)	37·5(35·5)	4·15 [b]
Co(sp)I_2	32·7(32·9)	4·9(4·8)	5·3(5·1)	45·6(46·4)	4·16 [b]
Cu(sp(Cl_2	48·7(49·6)	7·0(7·1)	7·6(7·6)	20·6(19·2)	1·91
Zn(sp)Cl_2	48·3(48·6)	7·0(7·1)	7·5(7·6)	18·5(19·1)	
Mn(sp)Cl_3	39·9(45·5)	6·5(6·6)	6·4(7·1)	23·9(26·9)	
Fe(sp)Cl_3	42·9(45·4)	6·7(6·6)	6·9(7·1)	24·1(26·5)	

[a] Calculated values in parentheses. [b] Corrected for temperature independent paramagnetism.

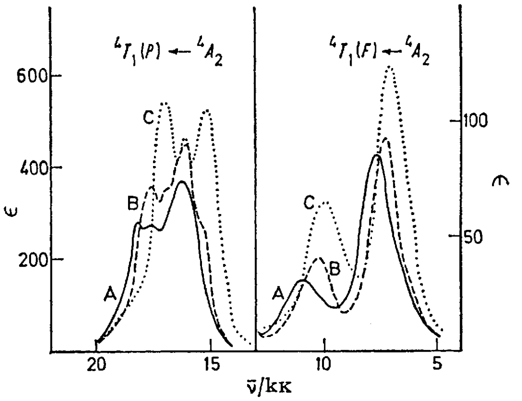


FIGURE 1 Electronic spectra in chloroform solution of A, [Co(sp)Cl_2]; B, [Co(sp)Br_2]; and C, [Co(sp)I_2]

The magnetic moment (1·91 B.M.) of [Cu(sp)Cl_2] falls within the range (1·8—2·0 B.M.) expected [9] for a mononuclear copper(II) complex. The electronic spectrum consists of one band at 7·7 kK (ε 260) and another at 12·4 kK (ε 270), which is consistent with a quasi-tetrahedral structure. A similar structure for the [Co(sp)X_2] complexes is indicated by their magnetic moments (Table 1) and electronic spectra (Figure 1). The absorption band intensities are too large for octahedral co-ordination and the magnetic moments are appreciably

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larger than expected[10] for either square planar (2·1—2·9 B.M.) or five-co-ordinate (1·9—2·5 B.M.) complexes of cobalt(II). By analogous criteria the magnetic moments (Table 1) and electronic spectra (Figure 2) of the [Ni(sp)X$_2$] complexes show that these also have a tetrahedral structure.

Models of the (—)-spartein complex with divalent transition metal ions indicate that the tetrahedral symmetry of the chromophore is lowered not only by the presence of two different pairs of ligand atoms but also by the steric constraints of the diamine ligand. For the metal–nitrogen bond distance of 1·95 Å, found in the dichloro-di(*p*-toludine)cobalt(II) complex,[11] the N–M–N bond angle in [M(sp)Cl$_2$] is *ca.* 95° and if that angle has the tetrahedral value the metal–nitrogen bond distance is reduced to *ca.* 1·7 Å. The two sets of ligand atoms and the bond-length or bond-angle distortion reduce the effective chromophoric symmetry to C_{2v} in which the degeneracy of the T_1 and T_2 tetrahedral *d*-electron states of the metal ion is completely lifted.

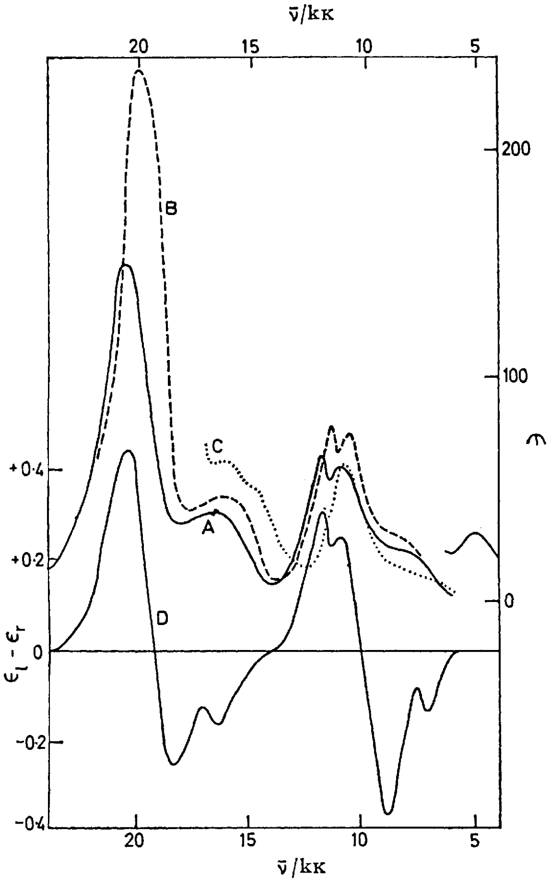

FIGURE 2 Upper curves: electronic spectra of A, [Ni(sp)Cl$_2$]; B, [Ni(sp)Br$_2$]; and C, [Ni(sp)I$_2$] in CHCl$_3$ solution and 4—6 kK in a KBr matrix (ε × 5); and lower curve, D, the c.d. spectrum of [Ni(sp)Cl$_2$] in CHCl$_3$ solution

Three components are found in a number of the band systems in the electronic spectra of the cobalt(II) and nickel(II) complexes, [M(sp)X$_2$] (Figures 1 and 2). These spectra are similar to those of the corresponding complexes[12] [M(tmdm)X$_2$], where tmdm is a tetramethyl-*N*,*N*,*N'*,*N'*-1,2- or -1,3-diamine, but are more fully resolved. The circular dichroism (c.d.) spectrum of the [Ni(sp)Cl$_2$] complex (Figure 2) reveals two component transitions, one at 9·0 kK and the other at 18·5 kK, which are weak and overlaid in the corresponding absorption spectrum. Each of these two components arises from a transition which is electric dipole forbidden but magnetic dipole allowed, with A_2 direct-product symmetry in C_{2v}. The $^3T_1$ tetrahedral ground term of nickel(II) gives the C_{2v} components, $^3A_2$, $^3B_1$, and $^3B_2$, whereas the lowest excited term, $^3T_2$, gives components with $^3A_1$, $^3B_1$, and $^3B_2$ symmetry. Accordingly the magnetic-dipole transitions represent $^3B_1 \longleftrightarrow {}^3B_2$ intercombinations, the one at 9·0 kK from the $^3T_2$ manifold and the other at 18·5 kK from the $^3T_1(P)$ tetrahedral term. The electronic ground state of [Ni(sp)Cl$_2$] may have $^3B_2$ and not $^3B_1$ symmetry, as shown in the approximate energy-level diagram of this complex (Figure 3), and in that event the excited $^3B_2$ states are relabelled $^3B_1$.

With these assignments the three C_{2v} components of the $^3T_1(P)$ nickel(II) term in [Ni(sp)Cl$_2$] are located at 16·5, 18·5, and 20·5 kK (Figure 2). The c.d. spectrum shows that rotational strengths of the individual components, R_i, follow the sum-rule, $\Sigma_i R_i = 0$, as expected for the effect of a weak dissymmetric field, due to the carbon and hydrogen atoms of (—)-spartein, superimposed upon the relatively strong C_{2v} perturbation. At lower energies the doublet observed in both the absorption and the c.d. spectrum at 12·0 and 11·2 kK is ascribed to transitions to the mixed C_{2v} states, $^3A_2$ and $^1A_2$, arising from the tetrahedral nickel(II) terms, $^3A_2$ and ^1E, respectively. Two of the components of the tetrahedral $^3T_2$ nickel(II) term are identified by the c.d. bands at 9·0 and 7·2 kK, and the third may be the weak band at 5 kK (ε 6) observed with [Ni(sp)Cl$_2$] in a KBr matrix (Figure 2). Alternatively the 5 kK band may represent the highest-energy component of the ground tetrahedral $^3T_1(F)$ term. A large splitting of that term (*ca.* 5 kK) is required to accommodate the observed spectra of the [Ni(sp)X$_2$] complexes (Figures 2 and 3) to values of the ligand field (*Dq*) and electron-repulsion (*B*) parameters found for analogous pseudo-tetrahedral nickel(II) complexes (Table 2). A C_{2v} splitting of the ground $^3T_1(F)$ term of a similar magnitude (4·8 kK) has been obtained[13] from a polarised single-crystal study of the analogous distorted tetrahedral complex, [Ni(Ph$_3$P)$_2$Cl$_2$].

The polarised single-crystal spectrum of the isostructural cobalt(II) complex, [Co(Ph$_3$P)$_2$Cl$_2$], also reveals large C_{2v} splittings of the tetrahedral T_1 *d*-electron terms of the metal ion.[14] The three C_{2v} components of the $^4T_1$ (*P*) term, centred on 15·4 kK, are split by 3·5 kK, and the corresponding components of the $^4T_1$ (*F*) term

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at 8·4 kK are split by 4·3 kK.[14] In the latter case the middle component at 8·0 kK (ε 25) is weak [14] relative to its neighbours at 6·4 kK (ε 110) and 10·7 kK (ε 60), and in the corresponding $^4T_1$ (*F*) manifold of the [Co(sp)X_2] complexes, where the splitting is smaller (3·0—3·5 kK), only two components are observed in the solution spectra (Figure 1), the middle component presumably being overlaid. The splitting of the $^4T_1$ (*P*) term of the [Co(sp)X_2] complexes in the 15—18 kK region (Figure 1) is similarly smaller (2 kK) than in [Co(Ph_3P)$_2Cl_2$]. Again the central of the three components has the smallest intensity (Figure 1), as also in the case [14] of [Co(Ph_3P)$_2Cl_2$].

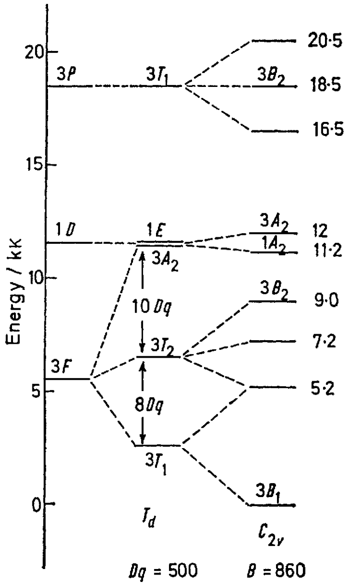

FIGURE 3 Partial energy level diagram for [Ni(sp)Cl_2]

TABLE 2

Values of *Dq* and *B* for pseudotetrahedral nickel(II) complexes

	Dq/cm^{-1}	*B*/cm^{-1}	Ref.
Ni(sp)Cl_2	500	860	*a*
Ni(sp)Br_2	470	830	*a*
Ni(Ph_3P)$_2Cl_2$	489	824	*b*
Ni(NCO)$_4^{2-}$	460	810	*c*
$NiCl_4^{2-}$	345	734	*d*

[a] This work. [b] R. J. Fereday, B. J. Hathaway, and R. J. Dudley, *J. Chem. Soc.* (*A*), 1970, 571. [c] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1964, 2790. [d] G. B. Smith, C. H. Liu, and T. R. Griffith, *J. Amer. Chem. Soc.*, 1964, **86**, 4796.

Values of *Dq* and *B* consistent with the observed solution spectra of the [Co(sp)X_2] complexes are recorded in Table 3, together with the values of the spin–orbit coupling parameter, λ, derived from the measured magnetic moments after correction for temperature independent paramagnetism.[15] The *Dq* and *B* values place the $^4T_2$ (*F*) term some 5 kK above the ground $^4A_2$ state of the [Co(sp)X_2] complexes. In a KBr matrix these complexes give a weak and broad absorption in the 4·5—5·55 kK region which is not present in the i.r. spectrum of the corresponding [Zn(sp)X_2] complex. The *Dq* and *B* values obtained in both the [Ni(sp)X_2] (Table 2) and the [Co(sp)X_2] series (Table 3) are rather large, exceeding in the cobalt(II) case the values proposed [16] for the tetrahedral [CoN_4] chromophore in [Co(benzimidazole)$_2$]. However, the π-bonding effects of an aliphatic diamine ligand are small, and possibly the steric constraints of the (—)-spartein molecule give rise to a shortened metal–nitrogen bond distance in the complex, producing a larger ligand field.

TABLE 3

Values of *Dq* and *B* for pseudotetrahedral cobalt(II) complexes

	Dq/cm^{-1}	*B*/cm^{-1}	$-\lambda$/cm^{-1}	Ref.
Co(sp)Cl_2	510	690	164	*a*
Co(sp)Br_2	490	690	175	*a*
Co(sp)I_2	470	680	174	*a*
Co(benzimidazole)$_2$	510	720	128	*b*
Co(Ph_3P)$_2Cl_2$	510	580		*c*
Co(pyridine)$_2Cl_2$	430	700		*d*
$CoCl_4^{2-}$	312	710	145	*e*

[a] This work. [b] M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, 1962, **84**, 1543. [c] C. Simo and S. Holt, *Inorg. Chem.*, 1968, **7**, 2655. [d] J. Ferguson, *J. Chem. Phys.*, 1959, **32**, 528. [e] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

EXPERIMENTAL

Metal halide (1 mmol) was dried over silica gel under vacuum for a few hours and quickly dissolved in boiling absolute ethanol (50 ml) to which triethylorthoformate (10 ml) had been added. The solution was boiled until the metal ion was completely dehydrated (5 min for the chlorides and up to 20 min for the bromides and iodides) when a solution of (—)-spartein (1·5 mmol) in absolute ethanol (50 ml) and triethylorthoformate (10 ml) was added. The mixture was boiled for a few minutes and filtered. It was sometimes necessary to extract the large amount of insoluble material produced with ethanol to obtain the co-precipitated complex. The ethanol solutions were cooled to 0 °C when the complexes crystallised. They were re-crystallised from boiling ethanol. A similar procedure was adopted with $FeCl_2$ and $MnCl_2$, oils being produced in each case. Complete removal of the ethanol and scratching caused these to solidify. No complexes could be obtained using the nitrate, perchlorate, or thiocyanate of nickel(II) nor could chromium(III) chloride be made to form a complex with (—)-spartein.

Absorption spectra were obtained on a Cary 17 spectrophotometer in EtOH or $CHCl_3$ solutions or in a KBr disc. C.d. spectra were obtained on a Jouan II instrument and on an instrument designed in this laboratory.[17] Magnetic moments were by the n.m.r. method,[18] the complex being dissolved in a $CHCl_3$–$CDCl_3$ mixture and using $CHCl_3$ as the external reference.

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