Five and Six-coordinated Chromium(II) Complexes with the Macrocyclic Ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane

FABRIZIO MANI

Istituto di Chimica Applicata, Università di Firenze, Florence, Italy

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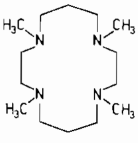
The ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) and chromium(II) salts give complexes with the formulae [CrX_2L] (X = Br, I), [CrClL]$BPh_4 \cdot 0.5CH_2Cl_2$, [CrXL]BPh_4 (X = Br, I, NCS), and [Cr(solv)L]$(BPh_4)_2$ (solv = acetonitrile, dimethylformamide). The coordination number and geometry of the complexes have been deduced on the basis of spectral, magnetic, and conductivity data. The neutral [CrX_2L] complexes are assigned a six-coordinated cis*-octahedral geometry in the solid state as well as in non-coordinating solvents, whereas five-coordinated species are present in dimethylformamide solution. All of the cationic [CrXL]BPh_4 complexes are five-coordinated with a distorted trigonal bipyramidal geometry, both in the solid state and in solution of a number of solvents. Presumably, the [Cr(solv)L]$(BPh_4)_2$ complexes have a distorted square pyramidal geometry in the solid state.*

Introduction

Amongst the saturated tetraazamacrocycles, the 1,4,8,11-tetraazacyclotetradecane and the N-methylated analogue have been thoroughly investigated as ligands towards bivalent and trivalent 3d metal ions [1, 2] owing to the rich coordination chemistry they give rise to, both in the solid state and in solution. As a part of our study into the coordination properties of simple macrocyclic ligands towards the early 3d bivalent ions [3], we decided to investigate the reactions between the ligands 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4-cyclam, I, hereafter indicated as L) and the chromium(II) ion.



I

We now report the synthesis and characterization of some chromium(II) complexes with the ligand Me_4cyclam. The reaction of cyclam and chromium(II) salts results in the instantaneous oxidation of the bivalent ion and in the formation of already known chromium(III) derivatives [4].

Experimental

In order to prevent oxidation, all reactions and operations were carried out under moisture-free nitrogen. Chromium(II) halides were prepared as already described [5]. The ligands were purchased from Strem Chemicals Inc. and were used without further purification.

In all of the preparations of the complexes stoichiometric amounts of the ligand and chromium(II) salts were employed. $CrBr_2L$ was prepared using dimethylformamide as solvent and di-n-butyl ether to promote the crystallization of the complex obtained as a blue microcrystalline product. CrI_2L was obtained by allowing an ethanolic solution of the reactants to boil until a blue crystalline product separated. Cr(solv)L$(BPh_4)_2$ (solv = dimethylformamide, acetonitrile) was obtained by the recrystallization of CrI_2L in the appropriate solvent, followed by the addition of a warm solution in ethanol of $NaBPh_4$. The crystalline products were obtained by allowing the solutions of the reactants to cool to room temperature. The dissolution of CrI_2L in dichloromethane, and the subsequent addition of $NaBPh_4$ in ethanol, results in the formation of the impure complex $CrILBPh_4$, since a variable (but generally small) amount of the iodide is replaced by the chloride ion originating from the decomposition of the solvent. Prolonged boiling of the $CrILBPh_4$ derivative in a CH_2Cl_2–C_2H_5OH mixture results in the formation of the mono-chloro adduct. For the synthesis of the $CrClLBPh_4 \cdot 0.5CH_2Cl_2$ and $CrXLBPh_4$ (X = Br, I, NCS) warm solutions in ethanol of the appropriate chromium(II) salts and $NaBPh_4$, and a solution in dichloromethane of the ligand were employed.

In all of the above preparations the solid compounds formed from the solutions were washed by decantation with appropriate solvents, filtered, washed with diethyl ether and finally dried by standing in a stream of dry nitrogen at 100 °C.

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TABLE I. Analytical Data for the Complexes.

	Found %			Calcd %		
	C	H	N	C	H	N
$[CrBr_2L]$	35.8	7.27	11.60	35.91	6.89	11.97
$[CrI_2L]$	29.5	5.94	9.67	29.91	5.74	9.97
$[CrClL]BPh_4 \cdot 0.5CH_2Cl_2$ [a]	65.8	7.98	8.03	65.54	7.57	7.94
$[CrBrL]BPh_4$ [b]	65.0	7.81	7.75	64.50	7.41	7.92
$[CrIL]BPh_4$	61.3	7.62	7.50	60.49	6.95	7.43
$[Cr(NCS)L]BPh_4$	67.9	7.77	10.00	68.30	7.64	10.21
$[Cr(CH_3CN)L](BPh_4)_2$	77.8	8.05	7.19	77.80	7.65	7.09
$[Cr(DMF)L](BPh_4)_2$	76.1	8.15	6.71	76.54	7.80	6.87

[a] Cl: found 10.2, calcd 10.04. [b] Br: found 11.0, calcd 11.29.

TABLE II. Some Physical Data for the Complexes.

	μ_{eff}, μ_B [a]		Λ_M [b], S cm^2 mol^{-1}	State [c]	Electronic spectra, nm (ϵ molar for soln. in parentheses)
	(298 K)	(88 K)			
$[CrBr_2L]$	4.74			R	670
			2	$MeCl_2$	655 (122)
			89	DMF	660 (111)
$[CrI_2L]$	4.74			R	630
			3	$MeCl_2$	640 (127)
			133	DMF	600 (66)
$[CrClL]BPh_4 \cdot 0.5CH_2Cl_2$	4.72	4.66		R	550 sh, 650
			24	$MeCl_2$	675 (110)
			99	Me_2CO	685 (90)
			51	DMF	670 (84)
$[CrBrL]BPh_4$	4.66	4.68		R	590 sh, 660
			19	$MeCl_2$	680 (120)
			100	Me_2CO	675 (112)
			60	DMF	660 (98)
$[CrIL]BPh_4$	4.65	4.60		R	640
			90	Me_2CO	660 (82)
			119	DMF	600 (70)
$[Cr(NCS)L]BPh_4$	4.70			R	630
			105	Me_2CO	630 (89)
$[Cr(CH_3CN)L](BPh_4)_2$	4.75			R	555
			111	DMF	600 (68)
$[Cr(DMF)L](BPh_4)_2$	4.74			R	560, 610 sh
			112	DMF	600 (81)

[a] 1 $\mu_B = 9.27 \times 10^{-24}$ A m^2. [b] For *ca.* 10^{-3} mol dm^{-3} solutions in the same solvents as the corresponding spectra; reference values are quoted in ref. 9. [c] R = diffuse reflectance; $MeCl_2$ = dichloromethane, DMF = dimethylformamide, Me_2CO = acetone.

The analytical data are reported in Table I.

Magnetic, spectrophotometric and conductivity measurements were performed with apparatus already described [6] on samples contained in suitable airtight containers, filled in a dry-box under inert atmosphere.

Results and Discussion

The ligand Me_4cyclam (I, L) reacts with chromium(II) salts to give complexes having the formulae $[CrX_2L]$ (X = Br, I), $[CrClL]BPh_4 \cdot 0.5CH_2Cl_2$, $[CrXL]BPh_4$ (X = Br, I, NCS), and [Cr(solv)L]-

$(BPh_4)_2$ (solv = dimethylformamide, acetonitrile). All of the complexes have magnetic moments at room temperature indicative of a spin-free d^4 configuration (Table II).

The electronic spectra of the complexes (both in the solid state and in solution) are similar, showing only one absorption maximum in the range 550–680 nm (Table II). This cannot be taken as diagnostic of any definite stereochemistry. However, by the comparison of magnetic moments, electronic spectra and conductivity data, plausible coordination numbers and geometries can be deduced for the present chromium(II) complexes.

The $[CrX_2L]$ derivatives in CH_2Cl_2 solution are non-conductors and consequently must be six-coordinated. Since their absorption spectra in the same solvent are substantially similar to those of the solid compounds (Fig. 1), the $[CrX_2L]$ are likewise also six-coordinated in the solid state. Solutions in DMF of the bromo and iodo derivatives are 1:1 and 1:2 electrolytes, respectively (Table II). Moreover, the absorption spectrum in DMF of the bromo adduct is quite identical to the spectrum of $[CrBrL]BPh_4$, both in the solid state and DMF solution (Fig. 1); the iodo derivative has an absorption spectrum in DMF quite identical to that of $[Cr(DMF)L](BPh_4)_2$ in the same solvent (Fig. 2). These data can be reasonably interpreted by assuming that the $[CrX_2L]$ complexes become five-coordinated in DMF solution according to the following reactions

$$[CrBr_2L] \xrightarrow{DMF} [CrBrL]^+ + Br^-$$

$$[CrI_2L] \xrightarrow{DMF} [Cr(DMF)L]^{2+} + 2I^-$$

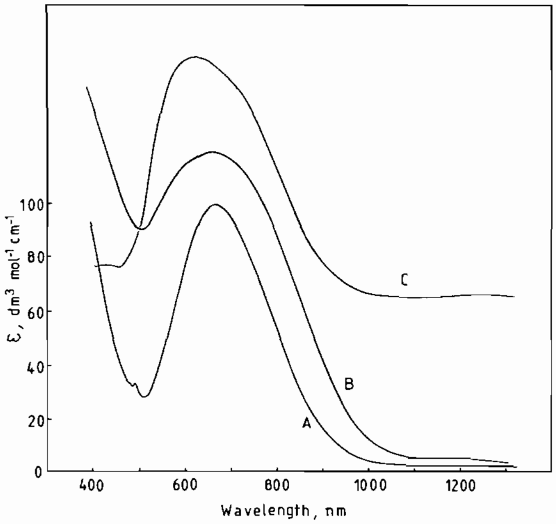


Fig. 1. Absorption spectrum in DMF of $[CrBrL]BPh_4$, A; reflectance spectra of $[CrBrL]BPh_4$, B; $[CrBr_2L]$, C.

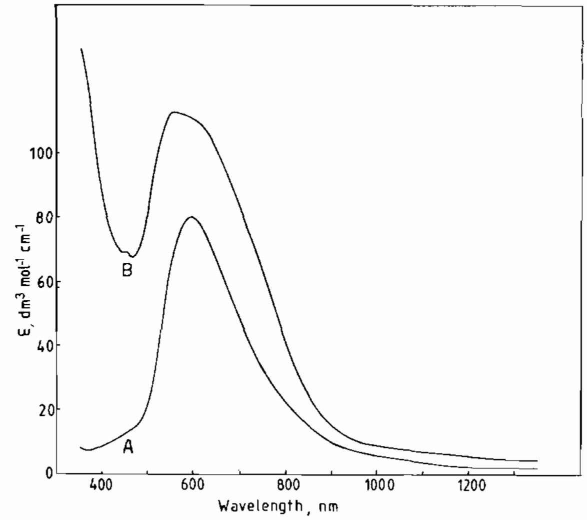


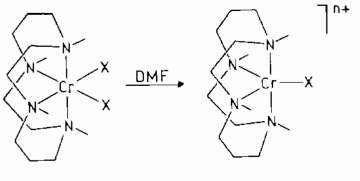
Fig. 2. Electronic spectra of $[Cr(DMF)L](BPh_4)_2$ in DMF solution (A) and as a solid (B).

The five coordination of the $[CrXL]BPh_4$ and $[Cr(solv)L](BPh_4)_2$ complexes, suggested by their stoichiometry, is based on magnetic and conductivity data. A six-coordinated halide-bridged structure for the solid $[CrXL]BPh_4$ derivatives can be rejected, since such a structure would lead to a magnetic interaction between chromium(II) ions and consequently to the temperature dependent magnetic behaviour always found in dimeric and polymeric chromium(II) compounds [5, 7]. Actually the $[CrXL]BPh_4$ complexes have magnetic moment values which are substantially temperature independent. On the other hand the complexes behave as 1:1 electrolytes in a number of solvents (Table II), with the exception of $[CrIL]BPh_4$ in DMF solution, and their absorption spectra are substantially similar to the solid reflectance spectra. $[CrIL]BPh_4$ behaves as 1:2 electrolyte in DMF solution; its absorption spectrum in the same solvent is quite identical to the spectra of $[CrI_2L]$ and $[Cr(DMF)L](BPh_4)_2$ in DMF solution. Spectral and conductivity data both indicate that the iodide is replaced by a molecule of the coordinating solvent. The $[Cr(solv)L](BPh_4)_2$ complexes are soluble in DMF where they behave as 1:2 electrolytes; as a consequence the solution structure could be five-coordinated (see later). As bridging DMF or CH_3CN are unlikely, a five coordination may also be assumed for the solid complexes.

A question remains unanswered by the above results, *i.e.* the coordination geometries of the six and five-coordinated complexes.

Structural determinations have revealed that $[Ni(N_3)L]ClO_4$ and $[ZnClL]ClO_4$ have a distorted square pyramidal structure, whilst electronic and ^{13}C n.m.r. spectra indicate that trigonal bipyramidal species are present in nitroethane solution [2]. Six-coordinated complexes in the solid state are unprecedented with the ligand Me_4cyclam, whereas *trans* octahedral $[Ni(CH_3CN)_2L]^{2+}$ are supposed to exist in acetonitrile solution [8].

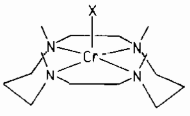
The electronic spectra of the $[CrX_2L]$ complexes are quite different in frequency and shape from the well known spectra of *trans*-octahedral chromium(II) complexes [3a]. Therefore it seems reasonable to assume that the solid $[CrX_2L]$ complexes, as well as their solutions in non-coordinating solvents, have a *cis* octahedral structure with the ligand arranged in a folded conformation (II). The ionization of one bromine in DMF solution, and the replacement of both iodines by one molecule of DMF, results in a five-coordinated structure (III) reconducible to the trigonal bipyramidal limiting geometry. Such a structure lessens the steric hindrance between the fifth donor group and the two CH_3 groups, and consequently is favoured over the square pyramidal geometry. A trigonal bipyramidal structure can be likewise assigned to the $[CrXL]BPh_4$ complexes on the basis of the close similarity of their spectra with those previously discussed. The same is true for the solution structures of $[Cr(solv)L](BPh_4)_2$.



II
X = Br, I

III
X = Br, n = 1
X = DMF, n = 2

As far as the structures of the solid $[Cr(solv)L](BPh_4)_2$ are concerned two considerations suggest that a distorted square pyramidal geometry (IV) could be more plausible than the trigonal bipyramidal one. It has been pointed out that the arrangement of the ligand in the structure IV prevents the bonding of the sixth ligand in the other axial position, owing to steric hindrance reasons [2]. Only the monosolvento adducts $[Cr(solv)L](BPh_4)_2$ were isolated in spite of the large excess of the coligand DMF and CH_3CN (see Experimental) which are, moreover, better ligands than Br^- and I^- which, on the contrary, give bis-adducts $[CrX_2L]$. The absorption maxima in the spectra of the solid $[Cr(solv)L](BPh_4)_2$ are higher in energy than those of the solutions in DMF (Fig. 2 and Table II), thus suggesting that the structures of the solid compounds and of DMF solutions are not strictly the same. On the other hand the formation of six-coordinated bis-solvento derivatives in DMF solutions is unlikely since the solutions absorb at lower energies when compared with the solid compounds.



IV

The energy difference between structures III and IV is known to be low [2] and it is reasonable to assume that crystal lattice forces make a square pyramidal geometry preferable to a trigonal bipyramidal one in the case of neutral coligands. In this respect it must be pointed out that the structures of the present chromium(II) complexes are actually rather distorted from the octahedral, trigonal bipyramidal and square pyramidal limiting geometries, as shown by their electronic spectra which do not differ from each other as much as one could expect if the complexes had the true limiting geometries.

Acknowledgements

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References

1 E. K. Barefield and F. Wagner, *Inorg. Chem.*, *12*, 2435 (1973); F. V. Lo Vecchio, E. Gore, D. H. Busch, *J. Am. Chem. Soc.*, *96*, 3109 (1974); L. Fabbrizzi, M. Micheloni and P. Paoletti, *J. Chem. Soc. Dalton*, 134 (1980); E. H. Curzon, N. Herron and P. Moore, *J. Chem. Soc. Dalton*, 574 (1980) and references therein.

2 M. J. D' Aniello, Jr., M. T. Mocella, F. Wagner, E. K. Barefield and I. C. Paul, *J. Am. Chem. Soc.*, *97*, 192 (1975); N. W. Alcock, N. Herron and P. Moore, *J. Chem. Soc. Dalton*, 1282 (1978).

3 a) A. Dei and F. Mani, *Inorg. Chem.*, *15*, 2574 (1976); b) A. Dei and F. Mani, *Inorg. Chim. Acta*, *19*, L39 (1976).

4 C. K. Poon and K. C. Pun, *Inorg. Chem.*, *19*, 568 (1980); J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, *4*, 109 (1970).

5 F. Mani and R. Morassi, *Inorg. Chim. Acta*, *36*, 63 (1979).

6 F. Mani and G. Scapacci, *Inorg. Chim. Acta*, *38*, 151 (1980) and reference therein.

7 A. Earnshaw, L. F. Larkworthy, K. C. Patel and B. J. Tucker, *J. Chem. Soc.*, 2209 (1977); M. M. Khamar, L. F. Larkworthy and M. H. O. Nelson-Richardson, *Inorg. Chim. Acta*, *28*, 245 (1978) and references therein.

8 N. Herron and P. Moore, *J. Chem. Soc. Dalton*, 441 (1979).

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