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Registry No. $(OCH_2CH_2NH)_2PH$, 1491-22-1.

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Existence of Two Isomeric Forms of Chromium(II) Complexes with Saturated Macrocyclic Ligands

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During the last 15 years a large number of 3d metal complexes with macrocyclic ligands have been synthesized and studied, in order to better understand their peculiar chemical properties, which often have biochemical interest.[1] The remarkable capacity of macrocyclic tetraamine ligands for stabilizing 3d metal ions in their low oxidation states[2] prompted us to investigate the coordinating behavior of such ligands toward chromium(II) halides, whose coordination compounds so far reported are not very numerous, owing to their instability toward oxidation.

This note reports the synthesis and characterization of chromium(II) complexes with two tetradentate macrocyclic ligands, *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (hence indicated as $Me_2[14]aneN_4$, I) and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($Me_6[14]aneN_4$, II).

Some chromium(II) complexes with the latter ligand have been already reported,[3] but, to our knowledge, no detailed study on these complexes has been so far reported in literature.

Experimental Section

All reactions and operations were carried out under moisture-free nitrogen. Anhydrous chromium(II) halides, $Me_2[14]aneN_4$ and $Me_6[14]aneN_4$ were prepared as already described.[4-6]

The complexes were prepared by adding a concentrated dimethylformamide solution of the appropriate chromium(II) halide to the stoichiometric amount of the ligand dissolved in the minimum amount of the solvent. Upon mixing of the reactants, the solutions are intensely blue, but gradually they become purple with subsequent precipitation of crystalline products of the same colour. The rate of turning from blue to purple is temperature dependent and markedly diminishes as the temperature is lowered. With the ligand $Me_6[14]aneN_4$, by keeping the blue solutions at 0–5 °C with an external ice bath, crystalline blue products having the same analytical formula as the corresponding purple compounds have been obtained.

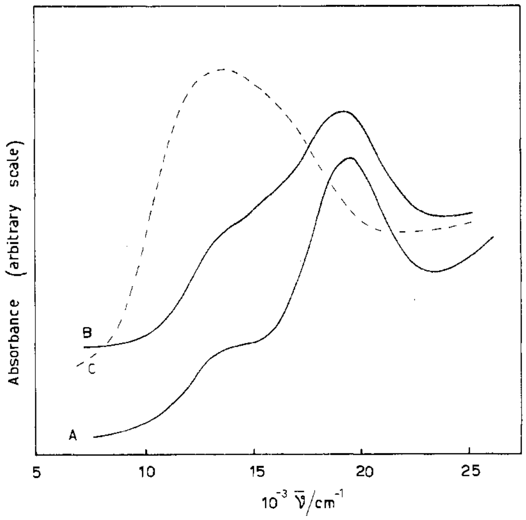
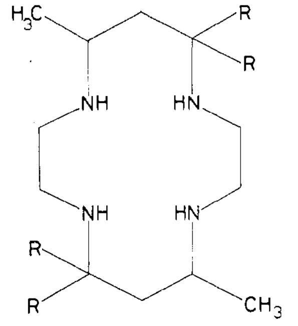


Figure 1. Diffuse reflectance spectra: A, $Cr(Me_2[14]aneN_4)Cl_2$; B, $Cr(Me_6[14]aneN_4)Cl_2$ (purple form); C, $Cr(Me_6[14]aneN_4)Cl_2$ (blue form).



I, R = H $L = Me_2[14]aneN_4$

II, R = CH_3 $L = Me_6[14]aneN_4$

Magnetic and spectrophotometric measurements were carried out using the apparatus already described[7] on samples contained in suitable airtight containers (Gouy tube, uv and ir cells) filled in a drybox under inert atmosphere.

Results and Discussion

Purple complexes having the general formula $CrLX_2$ ($L = Me_2[14]aneN_4$, X = Cl, Br; $L = Me_6[14]aneN_4$, X = Cl, Br, I) have been obtained. With the latter ligand blue complexes with the same analytical formula as the corresponding purple compounds have been also obtained. All of the complexes reported here, which are listed in Table I together with their elemental analyses, are sensitive to aerial oxidation and atmospheric moisture. The complexes are sparingly soluble in the common organic solvents with the exception of dichloromethane and 1,2-dichloroethane; however, in spite of the care employed to prevent oxidation, these solutions decompose in a short time so that physical measurements are practically precluded.

Magnetic and electronic spectral data are reported in Table I. All of the complexes are high spin with effective magnetic moments at room temperature in the range usually found for four unpaired electrons.

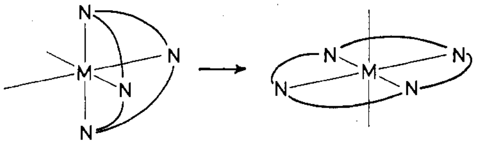
Table I. Analytical and Physical Data

Compd	Color	% found C	% found H	% found N	% found Cr	% calcd C	% calcd H	% calcd N	% calcd Cr	μ_{eff} (295 K), μ_B	Absorption max, 10^{-3} $\bar{\nu}$/cm^{-1}
$Cr(Me_6[14]aneN_4)Cl_2$	Blue	47.1	8.6	13.9		47.17	8.90	13.75	12.76	4.82	14.1
	Purple	46.9	9.0	13.9	12.4					4.80	14.7 sh, 19.4
$Cr(Me_6[14]aneN_4)Br_2$	Blue	39.2	7.2	11.6		38.72	7.31	11.29	10.48	4.77	15.0, 18.2 sh
	Purple	38.7	7.5	11.3	10.4					4.82	15.0 sh, 20.4
$Cr(Me_6[14]aneN_4)I_2$	Blue	32.2	6.4	9.4		32.56	6.15	9.49	8.81	4.82	15.4, 20.3
	Purple	32.1	6.5	9.5	8.8					4.92	20.0
$Cr(Me_2[14]aneN_4)Cl_2$	Purple	40.8	8.1	15.9		41.03	8.03	15.95		4.87	14.3, 19.7
$Cr(Me_2[14]aneN_4)Br_2$	Purple	32.3	6.7	13.0		32.74	6.41	12.73		4.90	15.4, 19.6

The ligand field spectra of $Cr(Me_2[14]aneN_4)X_2$ and purple $Cr(Me_6[14]aneN_4)X_2$ derivatives (Table I, Figure 1) are quite similar to each other and are strictly correlatable to the spectra of previously reported tetragonally distorted hexacoordinate chromium(II) complexes.[8] It is suggested, therefore, that in the above complexes the macrocyclic ligands adopt a planar arrangement of the four nitrogen donor atoms, the halide ions occupying the trans axial positions of the distorted octahedron. As the ligand field strength of the axial donor atoms becomes weaker in the order Cl, Br, I, in comparison to that of in-plane donor atoms, the splitting of the octahedral ^5E ground term increases. Consequently the frequency of the lower energy band (which is assigned to the transition between the components in D_{4h} symmetry of the ^5E ground term) is shifted to higher energy in the order Cl, Br, I (Table I), which is opposite of the order of increasing ligand field strength of the halogens. A support to the hypothesis of a planar arrangement of the nitrogen atoms may come from the similarity of the infrared spectra in both the 3200–3100 and the 1350–800 cm^{-1} regions of the present chromium(II) complexes with those of the other 3d metal complexes with the same ligands, for which a trans structure has been well established.[1]

The electronic spectra of the blue forms of the $Cr(Me_6[14]aneN_4)X_2$ derivatives exhibit a broad asymmetric band with a more or less enhanced shoulder on the high-energy side of the main absorption (Table I, Figure 1). Their magnetic behavior, which is temperature independent in the range 84–295 K, seems to rule out the existence of a halo-bridged dimeric or polymeric structure, which would lead to an at least partial magnetic interaction between chromium(II) ions.[4b,8]

In the formation of some macrocyclic copper(II) complexes, Margerum and his co-workers[9] postulated the existence of a reaction step involving the rearrangement of the macrocyclic ligand from a folded to a planar coordination around the copper(II) ion (III). This reaction step is accompanied by a blue to red interconversion of the complexes.



III

It appears reasonable to us that an analogous mechanism could be also operative in order to explain the blue to purple interconversion of the chromous solutions (see Experimental Section) and the existence of two isomeric forms of the $Cr(Me_6[14]aneN_4)X_2$ complexes. It is proposed, therefore, that the blue isomers contain the macrocyclic ligand arranged in a folded form. Actually the infrared spectra of the blue compounds show a different number of absorptions in the ranges 3200–3100 and 1350–800 cm^{-1} and at different frequencies, as compared to those of the purple ones. The electronic spectra alone are not diagnostic of any definite stereochemistry; however, they are quite different in frequency and shape from those of the purple complexes: in particular the main absorption maxima are lower in energy by ca. 5000 cm^{-1}. These spectral features could be consistent with a five-coordinate trigonal-bipyramidal CrN_4X chromophore, the folded configuration of the ligand favoring, with respect to the planar one, a distorted trigonal-bipyramidal geometry. In this framework the two observed absorptions could be assigned as transitions between the split ^5D term in D_{3h} symmetry.[10] Although a cis hexacoordinate structure cannot be completely ruled out for these complexes, considerable support to the former hypothesis comes from the existence of a stable five-coordinate trigonal-bipyramidal copper(II) complex with the macrocyclic ligand *dl*-$Me_6[14]aneN_4$, with four nitrogens and a chlorine atom bonded.[11]

It should be finally noted that in the reaction of 3d metal ions with the *ms*-$Me_6[14]aneN_4$ ligand, only with copper(II) and chromium(II) has it been possible to isolate two isomeric species, which presumably correspond to two distinct reaction steps.[12] With the other bivalent metal ions only one complex species, containing the macrocyclic ligand in the planar arrangement, has been observed. This fact seems to suggest that the electronic configuration of these two ions plays a fundamental role in determining the reaction mechanism and stabilizing different isomeric forms.

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Registry No. $Cr(Me_6[14]aneN_4)Cl_2$ (blue form), 59982-88-6; $Cr(Me_6[14]aneN_4)Cl_2$ (purple form), 59982-89-7; $Cr(Me_6[14]aneN_4)Br_2$ (blue form), 59982-90-0; $Cr(Me_6[14]aneN_4)Br_2$ (purple form), 59982-91-1; $Cr(Me_6[14]aneN_4)I_2$ (blue form), 59983-10-7; $Cr(Me_6[14]aneN_4)I_2$ (purple form), 59983-11-8; $Cr(Me_2[14]aneN_4)Cl_2$ (purple form), 59983-12-9; $Cr(Me_2[14]aneN_4)Br_2$ (purple form), 59983-13-0.

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