Pergamon

PII: S0277-5387(96)00545-1

Polyhedron Vol. 16, No. 13, pp. 2223–2227, 1997
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0277-5387/97 $17.00+0.00

Preparation and characterization of transition metal complexes of 1,4,8,12-tetra-azacyclopentadecane ([15]aneN$_4$)

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(Received 21 October 1996; accepted 31 October 1996)

Abstract—The preparation and characterization of a variety of transition metal complexes of the macrocycle 1,4,8,12-tetra-azacyclopentadecane ([15]aneN$_4$) with Cr^{III}, Mn^{III}, Fe^{III}, Ni^{II}, Zn^{II} and Rh^{III} are described. IR and visible spectra of the complexes are reported. © 1997 Elsevier Science Ltd

Keywords: macrocycle; [15]aneN$_4$; metal complexes; synthesis; IR and UV–vis spectra.

The ligand [15]aneN$_4$ can be readily prepared by the procedure described by Barefield and Freeman [1]. The 10-nitro-10-methyl derivative (**2**) can also be easily synthesised in high yield by reaction of the copper(II) complex of 1,10-diamino-4,7-diazadecane (3,2,3-tet) with EtNO$_2$ and HCHO in the presence of the non-coordinating base Et$_3$N [2,3]. The copper(II) complex can be readily reduced with Zn/HCl to give **3** as the pentahydrochloride [4]. The crystal structure of this salt has recently been reported [5]. As a result 15-membered tetra-aza macrocycles are readily available. The coordination chemistry of cyclam ([14]aneN$_4$) has been extensively studied, but much more limited work has been published dealing with the 15-membered ring system. In the present paper we discuss the preparation and characterization of a range of complexes of Cr^{III}, Mn^{III}, Fe^{III}, Rh^{III}, Ni^{II} and Zn^{II}.

EXPERIMENTAL

Synthesis

The ligand 1,4,8,11-tetra-azacyclopentadecane (L) was purchased from Strem Chemicals or synthesized as described by Barefield and Freeman [1]. The compound can be recrystallized from hexane to give fine white needles, m.p. 99–100°C when pure. The ligand is somewhat hygroscopic. Found: C, 61.4; H, 12.3; N, 26.2. Calc. for $C_{11}H_{26}N_4$: C, 61.6; H, 12.2; N, 26.2%.

[MnLCl$_2$]Cl·2H$_2$O. The ligand (0.25 g, 1.17 mmol) and MnCl$_2$·4H$_2$O (0.25 g, 1.26 mmol) were added to methanol (35 cm^3). Air was bubbled through the brown solution for 18 h, during which time the colour slowly darkened. Addition of concentrated HCl (1.5 cm^3) immediately afforded a bright yellow precipitate, which was filtered off and washed with acetone then ether. The solid was dissolved in the minimum volume of hot HCl (*ca* 5 cm^3, 1 mol dm^{-3}). The solution was filtered and acetone and ether added until the onset of precipitation occurred. On refrigeration overnight, a bright yellow precipitate formed which was washed with acetone, then ether and dried *in vacuo*. Yield 0.32 g (66%). Found: C, 32.9; H, 7.7; N, 13.9. Calc. for $C_{11}H_{30}N_4Cl_3MnO_2$: C, 32.1; H, 7.4; N, 13.6%. The IR spectrum had $\nu(H_2O)$ 3405 and ν(NH) 3080 cm^{-1}.

[FeL(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$. To a solution of [Fe(MeCN)$_6$](CF$_3$SO$_3$)$_2$ [2] (0.28 mmol in 25 cm^3 of acetonitrile) was added the ligand (0.06 g, 0.28 mmol) dissolved in acetonitrile (5 cm^3) to give a yellow–red solution. A stream of dioxygen was passed through the solution for 30 min. During this time an aqueous solution of CF$_3$SO$_3$H was slowly added dropwise. The colour of the solution lightened to yellow. Ethanol and ether were then added and the solution refrigerated overnight to give a yellow precipitate. The precipitate was filtered off, washed with ether and dried *in vacuo*. Yield 0.11 g (52%). Found: C, 21.9; H, 4.0; N, 7.3. Calc. for $C_{14}H_{30}N_4F_9FeO_{11}S_3$: C, 22.3; H, 4.0; N,

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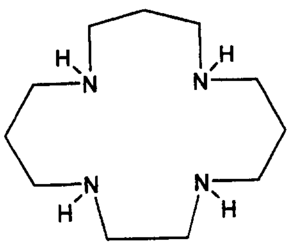

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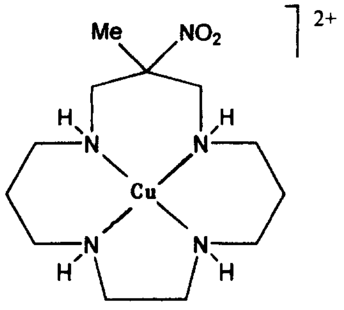

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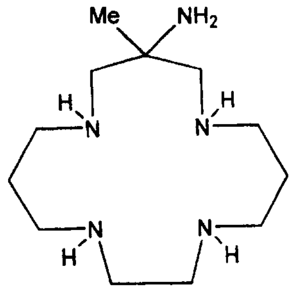


(3)

7.4%. The IR spectrum had $\nu(H_2O)$ 3487, ν(NH) 3130 and bands due to $CF_3SO_3^-$ at 1255, 1173, 1034 and 642 cm^{-1}.

$[RhLCl_2](ClO_4)_2$. The ligand (0.16 g, 0.75 mol) and $RhCl_3 \cdot 3H_2O$ (0.20 g, 0.76 mol) were added to ethanol (20 cm^3) and the solution refluxed for 45 min. After this time the yellow solution was filtered hot and a solution of $LiClO_4$ (0.10 g, 0.94 mmol) in ethanol (5 cm^3) added. The yellow solid which formed was filtered off, washed with portions of cold ethanol, then ether and dried *in vacuo*. Yield 0.35 g (86%). Found: C, 27.2; H, 5.5; N, 11.1. Calc for $C_{11}H_{26}N_4Cl_3O_4Rh$: C, 27.1; H, 5.4; N, 11.5%. The IR spectrum had ν(NH) 3219 and perchlorate bands at 1074 and 623 cm^{-1}.

$[NiL](ClO_4)_2$. The ligand (0.20 g, 0.94 mmol) and nickel(II) perchlorate hexahydrate (0.34 g, 0.94 mmol) were dissolved in ethanol (15 cm^3) and the solution heated on a steam bath for 10 min. Two drops of perchloric acid (75%) were added and the brown–orange solution heated for a further 10 min. On cooling an orange crystalline solid deposited. The crystals were filtered off, washed with ethanol then ether and dried *in vacuo*. Yield 0.25 g (57%). Found: c, 28.2; H, 5.5; N, 12.3. Calc. for $C_{11}H_{26}N_4Cl_2NiO_8$: C, 28.0; H, 5.6; N, 11.9%. The IR spectrum had ν(NH) 3208 and perchlorate bands at 1140, 1105 and 635 cm^{-1}.

Trans-$[NiL(OH_2)_2](ClO_4)_2$. In aqueous solution the yellow planar complex $[NiL](ClO_4)_2$ is converted to the purple *trans*-diaqua complex. The process is quite slow and can be monitored by following the decay of the 450 nm band in the visible spectrum due to the planar complex. On standing in air, a purple crystalline solid deposited from the aqueous solution. The solid was filtered off, washed with ethanol, then ether and dried *in vacuo*. Found: C, 26.2; H, 5.7; N, 11.1. Calc. for $C_{11}H_{30}N_4Cl_2NiO_{10}$: C, 26.0; H, 5.95; N, 11.0%. The IR spectrum had $\nu(H_2O)$3445, ν(NH) 3239 and perchlorate bands at 1107 and 635 cm^{-1}.

Cis-$[NiL(en)](ClO_4)_2$. The complex $[NiL](ClO_4)_2$ (0.15 g, 0.32 mmol) was dissolved in CH_3NO_2 (5 cm^3) and 1,2-diaminoethane (0.04 g, 0.66 mmol) in nitromethane (3 cm^3) added slowly with stirring. The solution immediately changed colour from orange to purple. On standing at room temperature for several hours purple crystals formed. The crystals were filtered off, washed with cold ethanol then ether and dried *in vacuo*. Yield 0.15 g (88%). Found: C, 28.95; H, 6.4; N, 15.9. Calc. for $C_{13}H_{34}N_6Cl_2NiO_8$: C, 29.3; H, 6.45; N, 15.8%. The IR spectrum had $\nu(NH_2)$ 3375, 3302, ν(NH) 3250, 3158 and perchlorate bands at 1102 and 627 cm^{-1}.

Trans-$[CrLCl_2]Cl \cdot HCl \cdot H_2O$. The ligand (0.20 g, 0.94 mmol) and $CrCl_3 \cdot 6H_2O$ (0.25 g, 0.94 mmol) were separately dissolved in DMF. The solutions were boiled for 15 min to expel all water and cooled to *ca* 100°C and the ligand added to the Cr^{III} solution. The solution changed colour from violet to green and the DMF removed by boiling. The resulting green powder was washed with acetone before dissolving in hot dilute HCl (3 cm^3), followed by addition of concentrated HCl (3 cm^3). On refrigeration overnight green crystals formed, which were filtered off, washed with acetone then ether and dried *in vacuo*. Yield 0.20 g, (50%). Found: C, 31.0; H, 6.6; N, 12.95. Calc. for $C_{11}H_{29}N_4Cl_4CrO$: C, 30.9; H, 6.85; N, 13.1%.

Trans-$[CrL(NCS)_2]Cl$. The complex *trans*-$[CrLCl_2]Cl \cdot HCl \cdot H_2O$ (0.03 g, 0.07 mmol) was dissolved in hot 0.1 M acetic acid (2 cm^3) and a solution of KNCS (0.10 g, 1.03 mmol) in water (5 cm^3) added. The resulting mixture was heated on a steam bath for 30 min, during which time the colour of the solution changed from green to red. The solution was evaporated to near dryness and was then refrigerated overnight. The red crystals which formed were filtered off, washed with water, ethanol then ether and dried *in vacuo*. Yield 0.02 g (68%). Found: C, 37.3; H, 6.4; N, 19.8. Calc. for $C_{13}H_{26}N_6ClCrS_2$: C, 37.35; H, 6.3; N, 20.1%. The IR spectrum had ν(NH) 3125 and $\nu(NCS^-)$ 2062 cm^{-1}.

Trans-$[CrL(OH)_2]^+$ *and* trans-$[CrL(OH_2)_2]^{3+}$. These complexes were prepared in solution and not isolated. The dihydroxo complex was prepared by dissolving the chloro complex in 0.1 M NaOH and stirring the solution for 15 min at room temperature. The colour of the solution changed from green to pink as hydrolysis occurred. The diaqua complex was prepared by acidification of the dihydroxo complex with 1.0 M nitric acid. The visible spectra of the two complexes were then determined.

Physical measurements

IR spectra were recorded as KBr discs on a Shimadzu IR-435 instrument. Electronic absorption spectra were obtained using a Perkin–Elmer Lambda 5 spectrophotometer.

RESULTS AND DISCUSSION

It has previously been shown [6] that Mn^{III} complexes of [15]aneN$_4$ can be prepared by the action of bromine on the corresponding Mn^{II} complex. Using this method $[MnLBr_2]^{2+}$ has been isolated as the bromide and PF_6^- salts [6]. Chan and Poon [7] have found that Mn^{III} complexes of cyclam ([14]aneN$_4$) can be prepared by bubbling air through a methanolic solution of the Mn^{II} complex for several hours and we have used this method in the present work. Thus, we were able to prepare the bright yellow $[MnLCl_2]Cl \cdot H_2O$ in 66% yield. The complex was found to have the high-spin d^4 configuration with $\mu_{eff} = 4.91$ BM at 18°C. For the high-spin complexes *trans*=[Mn(cyclam)X$_2$]$^+$ (X = Cl, Br, NCS, N$_3$) the magnetic moments fall within the range 4.79–5.03 BM [7]. The visible spectrum of the dichloro complex in water which will give the diaqua complex in solution has bands at 388 nm ($\varepsilon = 210$ dm^3 mol^{-1} cm^{-1}) and 304 nm ($\varepsilon = 920$), Table 1. Very similar spectra have been reported for the *trans*-[Mn(cyclam)X$_2$]$^+$ complexes [7]. Currently no crystallographic information is available on manganese(III) complexes of [15]aneN$_4$.

Nickel(II) *complexes*

Two nickel(II) complexes of [15]aneN$_4$ have been structurally characterized by X-ray crystallography, *trans*-[NiLCl$_2$] and *trans*-[NiL(NCS)$_2$] [8]. The structures are disordered in such a way that the five-membered chelate ring and the skew six-membered chelate ring are randomly interchanged in the crystal. In the present work we have characterized the planar yellow [NiL](ClO$_4$)$_2$, the purple octahedral [NiL(OH$_2$)$_2$](ClO$_4$)$_2$ and the folded purple *cis*-[NiL(en)](ClO$_4$)$_2$. The planar complex is readily prepared by reaction of the ligand with nickel(II) perchlorate in ethanol solution. The complex is a typical planar nickel(II) complex with a single *d–d* band at 450 nm ($\varepsilon = 80$ dm^3 mol^{-1} cm^{-1}) in nitromethane. In aqueous solution the planar complex slowly isomerises to the octahedral diaqua complex. The slow decay of the planar band at 450 nm in aqueous solu-

Table 1. Electronic spectra of complexes of [15]aneN$_4$

Complex	Solvent	λ_{max} (nm)	ε (dm^3 mol^{-1} cm^{-1})
$[MnLCl_2]Cl \cdot 2H_2O$	H_2O	388	210
		304	920
$[FeL(H_2O)_2](CF_3SO_3)_3$	H_2O	318	330
trans-$[RhLCl_2]ClO_4$	H_2O	510	sh
		418	81
$[NiL](ClO_4)_2CH_3$	NO_2	450	80
trans-$[NiL(H_2O)_2](ClO_4)_2$	H_2O	800	7
		570	9
		360	20
cis-$[NiL(en)](ClO_4)_2$	CH_3NO_2	735	7
		567	9
		356	18
trans-$[CrLCl_2]Cl \cdot HCl \cdot H_2O$	H_2O	591	25
		464	61
		417	64
trans-$[CrL(NCS)_2]Cl$	DMF	543	59
		465	78
		390	117
trans-$[CrL(OH)_2]^+$	0.1 M NaOH	505	49
		408	26
		331	35
trans-$[CrL(OH_2)_2]^{3+}$	H_2O^a	540	18
		456	66
		378	66

sh = shoulder.

^{a}The sodium hydroxide solution was neutralized with 1.0 M HNO$_3$.

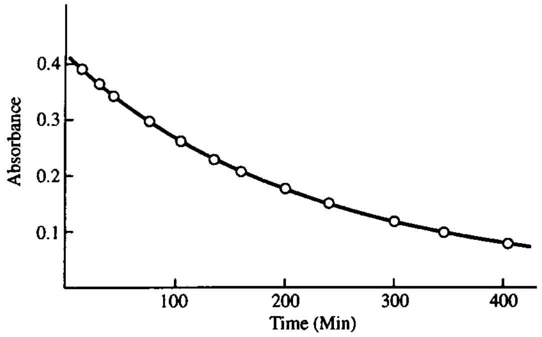


Fig. 1. Slow decay of the band due to the planar complex $[NiL]^{2+}$ at 450 nm in aqueous solution at 25°C. The complex concentration was 5×10^{-3} mol dm^{-3}. The rate constant for the isomerization process is 6.6×10^{-5} s^{-1} ($t_{1/2}$ = 173 min.).

tion at 25°C is shown in Fig. 1. The reaction is first order in the complex with $k = 6.6 \times 10^{-5}$ s^{-1}. This behaviour is very unusual. It has been suggested [9] that nearly concerted loss and addition of two water molecules occurs with $[Ni(cyclam)]^{2+}$,

$$[Ni(cyclam)]^{2+} + 2H_2O \rightleftharpoons [Ni(cyclam)(OH_2)_2]; \quad k_f, k_r$$

with the rate constants k_f and $k_r > 10^7$ s^{-1}. For *trans*-$[Ni(cyclam)(OH_2)_2]^{2+}$ the water exchange rate of 2.1×10^7 s^{-1} per water molecule corresponds to a minimum relaxation time of the planar ⇌ octahedral equilibrium of 80 ± 30 ns [19]. In the case of the larger 15-membered ring it seems probable that the planar complex isomerizes to the *cis*-diaqua complex which will require inversion of *sec*-NH centres. Such reactions are subject to specific acid and base catalysis and are very slow in neutral solution. Reaction of 1,2-diaminoethane with $[NiL](ClO_4)_2$ in nitromethane solution gave the purple *cis*-$[NiL(en)](ClO_4)_2$ in almost 90% yield establishing that folded *cis*-complexes with nickel(II) can be readily prepared. The visible spectra of the various nickel complexes prepared are summarized in Table 1.

Rhodium(III) *complexes*

There has been only one reported preparation of a rhodium(III) complex of the ligand. Bhattacharya [10] has described the preparation of *trans*-$[RhLCl_2]PF_6$. We have found that refluxing rhodium trichloride trihydrate with the ligand to ethanol for *ca* 1 h followed by addition of lithium perchlorate gives excellent yields of the yellow *trans*-$[RhCl_2]ClO_4$. The complex has λ_{max} 510 sh and 418 nm (ε = 81 dm^3 mol^{-1} cm^{-1}) in aqueous solution.

Iron(III) *complexes*

Iron(III) complexes of $[15]aneN_4$ of the type $[FeLX_2]^{n+}$ (X = MeCN, $n = 2$; X = NCS, CN, $n = 0$) and $[FeL(NO_2]^+$ have been prepared [11] by treating $[Fe(MeCN)_6](CF_3SO_3)_2$ with the ligand followed by addition of KX or $NaNO_2$. We have found that reaction of $[Fe(MeCN)_6](CF_3SO_3)_2$ [11] with the ligand followed by oxidation with dioxygen gives the yellow iron(III) complex $[FeL(OH_2)_2]^{3+}$, which can be crystallized as the triflate salt.

Zinc(II) *complexes*

A number of zinc(II) complexes of the ligand have been characterized by X-ray crystallography, including *trans*-$[ZnL(NCS)_2]$ [12] and the trimeric $[(ZnL)_3(CH_3OCO_2)_2](ClO_4)_4$ [13] containing the methylcarbonate ligand which bridges two $[ZnL]^{2+}$ moieties. Several methods have been used to prepare zinc(II) complexes of the ligand [14–16]. We have found that reaction of the ligand with zinc(II) perchlorate hexahydrate in methanol followed by addition of some concentrated HCl gave the colourless $[ZnL][ZnCl_4] \cdot H_2O$ in over 90% yield.

Chromium(III) *complexes*

The reaction of macrocyclic tetra-aza ligands with $[CrCl_3(DMF)_3]$ prepared *in situ* by boiling $CrCl_3 \cdot 6H_2O$ with DMF provides a useful method for the synthesis of chromium(III) complexes [17]. Swisher and co-workers [18] have prepared *trans*-$[CrLCl_2]Cl \cdot 2H_2O$ by oxidation of the chromium(II) complex. We have found that reaction of $[CrCl_3(DMF)_3]$ with the ligand in DMF solution followed by addition of concentrated HCl provide a rapid method for the synthesis of the green *trans*-$[CrLCl_2]Cl \cdot HCl \cdot H_2O$. If the reaction is carried out without the addition of HCl the green *trans*-$[CrLCl_2]Cl$ can be isolated directly. This latter complex is a 1 : 1 electrolyte in water with Λ_M = 94 S cm^2 mol^{-1} at 25°C in water with λ_{max} 593 (ε = 34 dm^3 mol^{-1} cm^{-1}), 462 (ε = 82) and 415 (ε = 88). Reaction

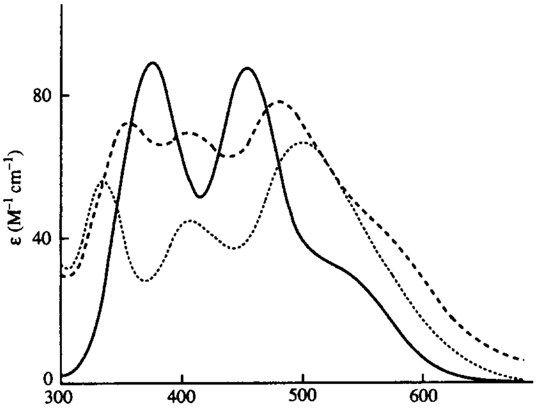
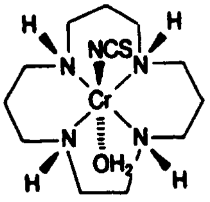


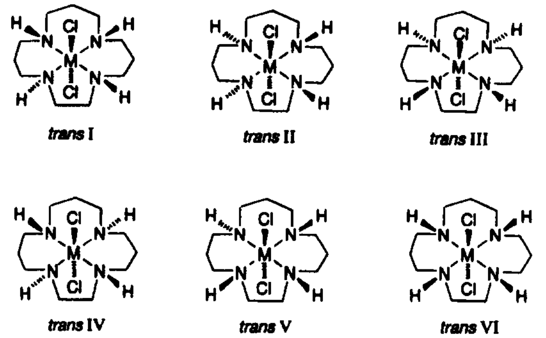
Fig. 2. UV–vis spectra for chromium(III) complexes of $[15]aneN_4$, *trans*-$[CrL(H_2O)_2]^{3+}$ (——), *trans*-$[CrL(H_2O)(OH)]^{2+}$ (– – –) and *trans*-$[CrL(OH)_2]^+$ (· · ·).



(4)

of the dichloro complex with KNCS in aqueous solution gave red crystals of the *trans*-[CrL(NCS)$_2$]Cl. Such anion metathesis reactions can be used to prepare a variety of derivatives. The spectra of the three complexes *trans*-[CrL(OH$_2$)$_2$]$^{3+}$, *trans*-[CrL(OH)(OH$_2$)]$^{2+}$ and *trans*-[CrL(OH)$_2$]$^+$ prepared by hydrolysis of the dichloro complex in aqueous solution are shown in Fig. 2. The crystal structure of [CrL(OH$_2$)NCS](NCS)$_2$ has been reported [18]. The compound has the *trans* VI configuration (**4**) with all of the *sec*-NH groups "up" on the same side as the NCS$^-$ ligand.

For complexes of the type *trans*-[MLX$_2$]$^{n+}$ six diastereoisomers are possible due to the presence of the four chiral *sec*-NH centres in the non-centrosymetric molecule. The possible diastereoisomers are shown in Fig. 3. In the centrosymetric cyclam ring system five diastereoisomers can occur *trans* I to *trans* V. The *trans* III structure is favoured as this arrangement gives rise to chair six-membered rings and *gauche* give-membered rings. In the 15-membered ring system the various diastereoisomers appear to have rather similar energies and no particular ring conformation appears to be particularly favoured. This view is supported by molecular mechanics calculations.


trans I **trans II** **trans III**

trans IV **trans V** **trans VI**

Fig. 3. Possible diastereoisomers of complexes of the type *trans*-[MLCl$_2$]$^{n+}$ (L = [15]aneN$_4$).

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