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A Tetra-aza Macrocycle Derived from (+)–Pulegone. Synthesis and Characterization of Copper(II) and Cobalt(III) Complexes

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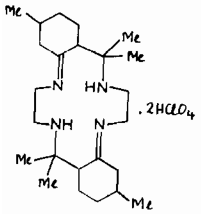
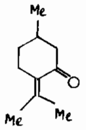
The reaction of monohydroperchlorate salts of diamines (*e.g.* ethylenediamine) with α,β-unsaturated ketones has provided a useful synthetic route to a variety of alkyl substituted tetra-aza macrocycles [1, 2]. In the present paper we describe the synthesis of the new macrocyclic ligand (I) derived from (+)–pulegone(II) and characterisation of a number of copper(II) and cobalt(III) complexes of the chiral macrocycle.



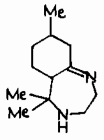
(I)



(II)

Experimental

(+)–Pulegone (Aldrich, 6.09 g, 0.04 mol) was added to a mixture of ethylenediamine·2HClO$_4$ (2.66 g, 0.02 mol) and ethylenediamine (1.2 g, 0.02 mol) in dry methanol (30 cm^3) at 0–5 °C. The mixture was stirred for 4 h, then the methanol removed *in vacuo* (rotatory evaporator). The residual thick pale yellow oil was diluted with ether and stored at –20 °C. The product crystallised over several days to give white crystals (1.5 g). The analytical sample was recrystallised from aqueous ethanol, m.p. 129–130 °C. The dihydroperchlorate salt of the macrocycle has a strong sharp band at 1660 cm^{-1} (νC=N), νNH at 3140 cm^{-1} and the characteristic perchlorate bands at *ca.* 1100 cm^{-1} (νCl–Oasym) and 625 cm^{-1} (δClO$_4$). *Anal.* Calc. for $C_{24}H_{46}Cl_2O_4N_8$: C, 48.89; H, 7.87; N, 9.50; Cl, 12.03. Found: C, 48.70; H, 7.95; N, 9.30; Cl, 11.90%. The reaction of pulegone with ethylenediamine (free base) does not give the macrocycle, but the diazapine derivative (III).



(III)

Preparattion of Complexes

The complex [CuL](ClO$_4$)$_2$ was prepared as follows. The ligand dihydroperchlorate (L·2HClO$_4$) (0.2 g) was dissolved in water (50 cm^3) and treated with an excess of copper(II) carbonate (0.3 g). The mixture was heated on a water bath for 1 h, then cooled and filtered. The filtrate was evaporated to small volume (*ca.* 3 cm^3), cooled in ice and treated with excess methanol. The reddish complex so obtained was filtered off and washed with methanol. The complex was purified by dissolving in the minimum quantity of water and reprecipitating with cold ethanol. It was washed with ethanol, then ether and dried *in vacuo. Anal.* Calc. for $C_{24}H_{44}N_4Cl_2O_8Cu$: C, 44.27; H, 6.81; N, 8.60. Found: C, 43.98; H, 6.69; N, 8.73%.

Trans-[CoLCl$_2$]ClO$_4$ was prepared as follows. The ligand dihydroperchlorate (0.59 g) was dissolved in methanol (10 cm^3) and a solution of cobalt(II) acetate tetrahydrate (0.25 g) in methanol (20 cm^3) added. The solution was heated on a steam bath for 1 h, then diluted to 100 cm^3 with aqueous methanol (1:1 v/v) and then aerated for 24 h. Concentrated HCl (5 cm^3) was then added and the solution evaporated to small volume on a steam bath to give green crystals which were filtered off and washed with ethanol *Anal.* Calc. for $C_{24}H_{44}N_4Cl_3O_4Co$: C, 46.65; H, 7.72; N, 9.07. Found: C, 46.97; H, 7.52; N, 9.60%. The complex is also readily prepared by reaction of freshly prepared Na$_3$[Co(CO)$_3$]3H$_2$O [11] with L·2HClO$_4$ in aqueous methanol followed by evaporation with conc. HCl.

Trans-[CoCl(L)NO$_2$]ClO$_4$. A solution of *trans*-[CoLCl$_2$]ClO$_4$ (0.31 g, 0.5 mmol) in hot methanol (10 cm^3) was heated with an equivalent of sodium nitrite (0.035 g, 0.5 mmol). The solution slowly turns brownish and cooling in ice gave fine crystals which were filtered, washed with cold ethanol, then ether and dried. *Anal.* Calc. for $C_{24}H_{44}N_5Cl_2O_6$-CO: C, 45.87; H, 7.06; N, 11.14. Found: C, 46.06; H, 6.86; N, 11.48%.

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TABLE I. Infrared Data for the Ligand and its Complexes.

Compound	νNH (cm^{-1})	νC=N (cm^{-1})	νClO_4 (cm^{-1})	νNO_2 (cm^{-1})
$L\cdot 2HClO_4$	3140	1660	(1100) (620)	–
$[CuL](ClO_4)_2$	3210	1670	(1090) (630)	–
$[CoLCl_2](ClO_4)_2$[a]	3180	1655	(1080) (620)	–
$[CoLCl(NO_2)](ClO_4)$[a]	3160	1655	(1100) 625	1400[c] 825[d]
$[CoL(NO_2)_2](ClO_4)$[a]	3130	1650	1100 625	1400[c] 825[d]

[a] These complexes have a *trans* stereochemistry. [c] ν_{asy} (NO_2). [d] ν(ONO).

Trans-$[CoL(NO_2)_2]ClO_4$ was prepared by heating *trans*-$[CoLCl_2]$ (0.31 g) in methanol with an excess of $NaNO_2$ (0.134 g). Cooling in ice gave fine yellow crystals which were washed with ethanol, then ether and dried *in vacuo*. *Anal.* Calc. for $C_{24}H_{44}N_6ClO_8Co$: C, 45.11; H, 6.94; N, 13.15. Found: C, 45.41; H, 6.64; N, 13.06%.

IR spectra were determined as discs in KBr on a Perkin-Elmer 457 spectrophotometer, Electronic spectra were determined on a Perkin-Elmer 402 instrument using water or acetonitrile as solvent. Conductivity measurements were made with a Portland conductivity meter Model P301 using 1×10^{-4} *M* solutions in water. NMR spectra were determined using a Bruker WP80 spectrometer using d_6-DMSO as solvent and TMS as internal reference.

Results and Discussion

The reaction of (+)–pulegone with ethylenediamine monohydroperchlorate (prepared *in situ* from the dihydroperchlorate and ethylenediamine) in methanol at 0–5 °C gives low yields (*ca.* 12%) of the macrocycle dihydroperchlorate salt ($L\cdot 2HClO_4$) (I). Although the yield is low, the synthesis provides a useful synthetic route to a chiral tetra-aza macrocycle (the starting materials are quite accessible). The synthesis is very dependent on the use of dry methanol and temperatures of 0–5 °C during the addition-condensation reaction, otherwise only starting materials are recovered.

The dihydroperchlorate salt of the macrocycle has the expected spectroscopic properties, with νC=N at 1660 cm^{-1} and νNH at 3140 cm^{-1}, the characteristic bands due to ionic perchlorate occur at 1100 and 620 cm^{-1}, Table I.

The ligand dihydroperchlorate salt reacts with an excess of copper(II) carbonate to give $[CuL](ClO_4)_2$ as reddish crystals. The complex is a 2:1 electrolyte in aqueous solution (Λ_M = 235 S cm^2 mol^{-1} at 25 °C) and the d–d spectrum has a single band at 500 nm (ϵ = 132 M^{-1} cm^{-1}). This band is very comparable to that observed [3] with $[Cu(tet\,a)(red)]^{2+}$ where λ_{max} = 500 nm (ϵ = 124 M^{-1} cm^{-1}) (tet *a* = C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), and [Cu(*trans*[14]diene)]ClO_4 λ_{max} 500 nm (ϵ = 110 M^{-1} cm^{-1}) (*trans*[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) [4].

Attempts to characterise a nickel(II) complex by reaction of nickel(II) carbonate with $L\cdot 2HClO_4$ in aqueous solution were only partially successful. A yellow low-spin planar complex was isolated, but gave poor analytical data. Incorporation of nickel(II) into tetra-aza macrocycles in aqueous solution can be relatively slow and it is presumed that under the conditions employed (water bath temperatures) considerable ligand decomposition occurred by a retro-Michael and/or imine hydrolysis. Macrocyclic dienes such as *trans*[14]diene exert a strong ligand field on nickel(II), thus the ligand field strength of this macrocyclic ligand has been calculated [5] to be 1569 cm^{-1}, making it one of the most strongly coordinating of the synthetic macrocyclic quadridentates on nickel(II). A low-spin, planar nickel(II) complex with L is therefore to be expected.

Metal complexes of the ligand have two chiral centres so that N-*meso* and N-*racemic* diastereoisomers are possible. Molecular models indicate that the N-*meso* configuration may be preferred in six coordinate complexes, since the N-*racemic* configuration leads to considerable steric crowding of one axial site by two axial methyl groups. Such

TABLE II. Electronic Spectra of the Complexes.

Complex	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
[CuL]$(ClO_4)_2$	500	132
	265	67,500
	245	70,600
[$CoLCl_2$]$(ClO_4)_2$[a]	625	81
	330(sh)	1,863
	272	34,400
[CoLCl(NO_2)](ClO_4)	485	142
	345	1,530
	222	29,900
[CoL$(NO_2)_2$](ClO_4)	447	244
	350	4,900
	260	26,800
	225	32,000

[a] In acetonitrile, all other complexes in aqueous solution.

considerations are probably of less importance for planar 4-coordinate complexes, and with *trans*[14] diene it is possible to characterise the N-*meso* and N-*racemic* diastereoisomers of the planar nickel(II) complex [6–8].

Reaction of the ligand dihydroperchlorate with cobalt(II) acetate in aqueous methanol followed by aerial oxidation and treatment with hydrochloric acid gives the green *trans*-$[CoLCl_2]^+$ cation, readily isolated as the perchlorate salt. This complex can also be prepared by reaction of L•2HClO$_4$ with $[Co(CO_3)_3]^{3-}$ in aqueous methanol followed by treatment with HCl. The *trans* configuration is consistent with the d–d spectrum, Table II with the $^1A_{1g} \rightarrow {}^1T_{1g}$ (in O_h) occurring at 625 nm (ϵ = 81 M^{-1} cm^{-1}). Metathesis reactions in methanol give the brown chloronitro complex and the yellow dinitro complex. The reaction of ethylenediamine monohydroperchlorate with α,β-unsaturated ketones appears to be fully stereospecific [1, 2] giving only the *trans*-diimine rather than mixtures of the *trans* and *cis*-diimines observed in some metal template cyclisations [9, 10]. As (+)–pulegone was used in the synthesis of the ligand, both cyclohexane ring methyl groups will lie on the same side of the macrocyclic plane. Two diastereoisomers arise due to the presence of the chiral nitrogen centres. The N-*meso* diastereoisomer (in which the N–H bonds lie on opposite sides of the macrocyclic plane) has no elements of symmetry (C_1), while the N-racemic diastereoisomer which has both N–H bonds on the same side of the ring will have C_2 symmetry.

^{1}H NMR studies of the diamagnetic cobalt(III) complex [CoL$(NO_2)_2$](ClO_4) in d_6-DMSO indicate two NH signals at 4.15 and 6.90 δ consistent with the N-*meso* diastereoisomer. Three methyl signals occur (all singlets) in the NMR spectrum, the highest field signal (0.92 δ) is assigned to the axial methyl of the *gem*-dimethyl group and the signal at 1.61 δ to the equatorial methyl of the *gen*-dimethyl group. The methyl group of the cyclohexane ring occurs as a sharp singlet at 2.42 δ. There appears to be no coupling with the ring hydrogen, possibly because it lies directly above this proton.

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References

1 N. F. Curtis and R. W. Hay, *J. Chem. Soc. Chem. Comm.*, 524 (1966).

2 R. A. Kolinski and B. Korybut-Daszkiewicz, *Inorg. Chim. Acta, 14,* 237 (1975).

3 B-F. Liang and C-S. Chung, *Inorg. Chem., 20,* 2152 (1981).

4 N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

5 C. R. Sperati, Ph.D. Thesis, The Ohio State University, 1971.

6 L. G. Warner, N. J. Rose and D. H. Busch, *J. Am. Chem. Soc., 90,* 6938 (1968); *89,* 703 (1967).

7 N. F. Curtis, Y. M. Curtis and H. J. K. Powell, *J. Chem. Soc. (A)*, 1015 (1966).

8 N. F. Curtis and Y. M. Curtis, *J. Chem. Soc. (A)*, 1653 (1966).

9 N. F. Curtis, *J. Chem. Soc.*, 4409 (1960).

10 M. Blight and N. F. Curtis, *J. Chem. Soc.*, 3016 (1962).

11 H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc., 82,* 5031 (1960).