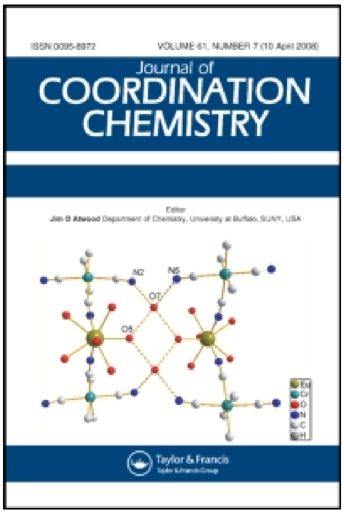

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ISOMERIZATION IN RHENIUM(V) COMPLEXES. THE ISOLATION AND CHARACTERIZATION OF *CIS* AND *TRANS* ISOMERS OF RHENIUM(V) COMPLEXES WITH DERIVATIVES OF 2-AMINO-1-CYCLOPENTENE-1-DITHIOCARBOXYLIC ACID

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The complexes *trans*-$ReOCl_3(PPh_3)$ (HL')·Me_2CO [HL' = 2-(*N*-ethylamino)-1- cyclopentenedithiocarboxylate and 2-(*N*-cyclohexylamino)-1-cyclopentenedithiocarboxylate], with the ligand HL' coordinated as a monodentate to rhenium(V) through the neutral thiocarbonyl sulfur atom in the position *trans* to the PPh_3 molecule, were prepared under reflux conditions in acetone by the reaction of *trans*-$ReOCl_3(PPh_3)_2$ with a molar excess of HL'. The products were isolated as light green precipitates from reaction solutions immediately after cooling to room temperature. The compounds *cis*-$ReOCl_3(PPh_3)$ (HL')·Me_2CO were isolated as dark green crystals from the filtrate on slow evaporation of the solvent at room temperature over a period of 2 days. Physicochemical, infrared, ^1H NMR and spectroscopic data are reported.

KEYWORDS: rhenium(V), substituted aminodithiocarboxylates, complexes, isomerization

INTRODUCTION

A specific goal in recent developments of nuclear medicine has been the design and synthesis of neutral oxotechnetium(V) and rhenium(V) complexes containing N_2S_2-donor ligands.[1,2] The ability of such compounds to cross the blood-brain barrier has been demonstrated,[3–5] and in order to improve both the uptake and/or the retention in brain tissue, many structural modifications of the ligand skeleton have been attempted.[6–9] Up to now, only saturated bis(aminethiol) ligands have been studied extensively.[1–7]

As part of a study to investigate the technetium(V) and rhenium(V) complexes formed by 2-amino-1-cyclopentene-1-dithiocarboxylic acid and its derivatives, we have isolated complexes of formula $ReOCl_3$ (PPh_3) (HL')·Me_2CO [HL' = 2-(*N*-ethylamino)-1-cyclopentenedithiocarboxylate (HECD) and 2-(*N*-cyclohexylamino)-1-cyclopentenedithiocarboxylate (HCCD); see Figure 1]. In principle, the ligands HL' may exist in three tautomeric forms (Figure 1), and they have the potential to coor-

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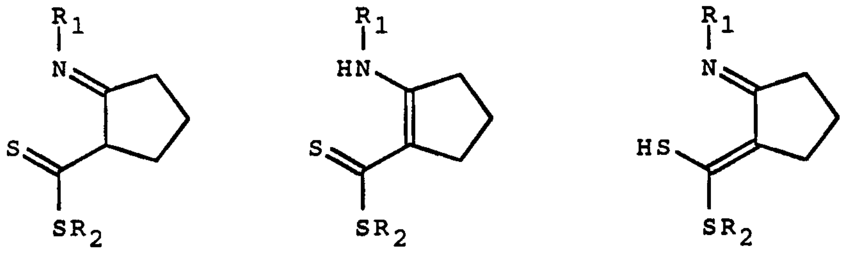

I II III

R_1	R_2	Abbvn
C_2H_5	CH_3	HECD
cyclohexyl	CH_3	HCCD

Figure 1 Ligands used in the study, with their possible tautomeric forms (HECD = 2-(*N*-ethylamino)-; HCCD = 2-(*N*-cyclohexylamino)-1-cyclopentenedithiocarboxylate).

dinate as bidentates (NS $^-$) to metal ions to yield products of formula $ReOCl_2(PPh_3)$ (NS). However, in a previous account we reported[10] the X-ray structure of *cis*-$ReOCl_3$ (PPh_3) (HECD)·Me_2CO, in which it was shown that coordination of HECD occurs as a monodentate through the neutral thiocarbonyl sulfur atom only, in the position *cis* to PPh_3, in a distorted octahedral complex. This *cis* product contrasts with the *trans* geometry of the phosphines in the starting complex *trans*-$ReOCl_3(PPh_3)_2$.

This paper describes the preparation and characterization of the compounds *cis*-$ReOCl_3$ (PPh_3) (HL′)·Me_2CO, and the properties of the *trans* isomers.

EXPERIMENTAL

Materials

Trans-$ReOCl_3(PPh_3)_2$ [11] and the ligands[12] HECD and HCCD were prepared according to literature procedures. All common laboratory chemicals were of analytical grade and were used without further purification. All solvents were dried and purified by standard methods.

Apparatus

Scientific instrumentation used in this study is the same as reported elsewhere.[13]

Synthesis of the Complexes

Trans-ReOCl$_3$ (PPh$_3$) (HL′)·Me$_2$CO [HL′ = HECD, HCCD]

The preparation was similar for both ligands HL′. *Trans*-ReOCl$_3$ (PPh$_3$)$_2$ (100 mg, 120 μmol) was suspended in 5 cm^3 of acetone. The ligands HL′ (240 μmol) were added, and the mixture was heated under reflux for 30 min. The initial pale green colour of the reaction solution turned to dark red, and after cooling to room temperature, the solution was filtered to give a light green, crystalline precipitate. The solids were washed with ethanol (3 × 2 cm^3) and acetone (1 × 3 cm^3) and dried under vacuum.

Cis-ReOCl$_3$ (PPh$_3$) (HL′)·Me$_2$CO [HL′ = HECD, HCCD].

The filtrate from the above preparations was left to evaporate slowly over a period of 2 days, with continual concomitant formation of dark green crystals. After removal by filtration, the crystals were washed three times with ethanol (2 cm^3).

A crystal structure determination[10] of dark green *cis*-ReOCl$_3$ (HECD)·Me$_2$CO (see Figure 2) showed that the ligand HECD coordinates to the metal *via* the neutral thiocarbonyl sulfur atom in a monodentate manner in a position *cis* to triphenylphosphine. All other experimental evidence shows that the light green precipitates obtained from the reaction solutions can be formulated as *trans*-ReOCl$_3$ (PPh$_3$) (HL′)·Me$_2$CO. Recrystallization and the growing of crystals for X-ray

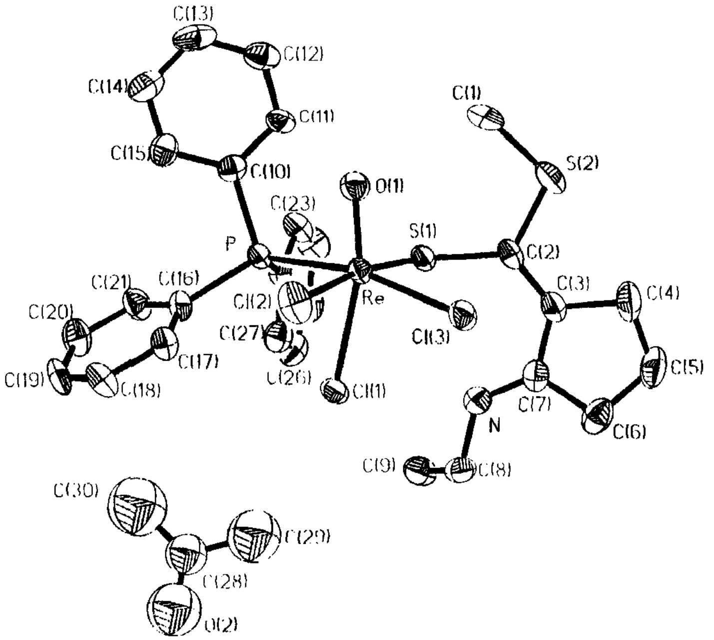

Figure 2 View of *cis*-[ReOCl$_3$ (PPh$_3$) (HECD)]·Me$_2$CO with thermal ellipsoids at 40% probablility level.

crystal structure analysis of the latter product was impossible due to isomerization to the *cis* isomer in all the solvents in which the *trans* product was soluble.

Physicochemical, infrared, ^{1}H NMR and electronic spectroscopic data are presented in Tables 1 to 4, respectively.

RESULTS AND DISCUSSION

Synthesis

The complexes *trans*-$ReOCl_3$ (PPh_3) (HL')·Me_2CO [HL' = HECD, HCCD, Figure 1], with the ligand HL' coordinated *trans* to the PPh_3 molecule, were prepared under reflux conditions in acetone by mixing *trans*-$ReOCl_3$ $(PPh_3)_2$ with an excess of the appropriate ligand HL'. The products were isolated as light green precipitates from reaction solutions immediately after cooling to room temperature. The complexes *cis*-$ReOCl_3$ (PPh_3) (HL')·Me_2CO were isolated as dark green crystals from the mother liquor on slow evaporation of the solvent at room temperature. The *cis* isomers were also isolated in reasonable yields (75%) when the recrystallization of *trans*-$ReOCl_3$ (PPh_3) (HL')·Me_2CO was attempted in acetonitrile. When the same reaction was carried out under the same conditions in ethanol, the product *trans*-$ReOCl_2$ (OEt) (PPh_3) (HL') was isolated. Reactions of ligands HL' with (*n*-Bu_4N) [$MOCl_4$] (M = Tc, Re) in acetone and ethanol led to the isolation of very impure products, which were impossible to purify by ordinary chemical means.

All the complexes prepared in this study are insoluble in non-polar and weakly polar organic solvents like benzene, dichloromethane, alcohols, toluene, acetone, diethyl ether and THF, and they are poorly soluble in chloroform, acetonitrile and DMF, in which they dissolve to give orange solutions. The complexes are all diamagnetic in the solid state and in solution.

In addition to the single-crystal X-ray determination[10] of *cis*-$ReOCl_3(PPh_3)$ (HECD)·Me_2CO, the complexes have been characterized by elemental analysis, infrared spectroscopy and proton NMR spectroscopy. Conductivity measurements have been performed for all the complexes (Table 1).

Table 1 Physicochemical properties of the complexes.

Complex	Colour	Mpt (°C)	Conductivity†	Analysis*(%)				Yield (%)
				C	H	N	Cl	
cis-$ReOCl_3$ (PPh_3) (HECD)·Me_2CO	dark green	173	43	43.70 (43.40)	4.52 (4.37)	1.48 (1.69)	12.73 (12.81)	18
trans-$ReOCl_3$ (PPh_3) (HECD)·Me_2CO	light green	144 (dec)	48	43.67	4.79	1.58	12.64	61
cis-$ReOCl_3$ (PPh_3) (HCCD)·Me_2CO	dark green	163	51	45.93 (46.23)	4.83 (4.68)	1.54 (1.59)	12.21 (12.04)	21
trans-$ReOCl_3$ (PPh_3) (HCCD)·Me_2CO	light green	166	29	46.33	4.79	1.68	12.33	64
trans-$ReOCl_2$ (OEt) (PPh_3) (HCCD)	brown	175	46	47.66 (47.48)	4.01 (3.98)	1.90 (1.68)	8.73 (8.49)	82

†In DMF; values in $ohm^{-1}cm^2mol^{-1}$. *Calculated in parentheses.

Table 2 Selected infrared data for the complexes (cm^{-1})[†].

Complex	ν(Re=O)	ν(C···N)	ν(N–H)	ν(Re–Cl)	ν(C=S)[§]
cis-$ReOCl_3$ (PPh_3) (HECD)·Me_2CO	974	1503	3141	316;289	1254
trans-$ReOCl_3$ (PPh_3) (HECD)·Me_2CO	972	1503	3142	326;290	1250
cis-$ReOCl_3$ (PPh_3) (HCCD)·Me_2CO	976	1501	3140	318;289	1258
trans-$ReOCl_3$ (PPh_3) (HCCD)·Me_2CO	976	1503	3142	318;291	1258
trans-$ReOCl_2$ (OEt) (PPh_3) (HCCD)*	947	1481	3138	320	1255

[†] KBr pellets. * δ(OEt) at 909 cm^{-1}. [§] At 1265 cm^{-1} in HECD and at 1275 cm^{-1} in HCCD.

All complexes show intense and characteristic infrared stretching vibrations consistent with the exhibited core. The $ReOCl_3$ (PPh_3) (HL′) species show ν (ReO) in the narrow region 972–976 cm^{-1}. The complex $ReOCl_2$ (OEt) (PPh_3) (HCCD) shows a medium intensity band at 947 cm^{-1} [ν (Re=O)], and a strong peak at 909 cm^{-1} characteristic of the ethoxy deformation mode. Evidence for the monodentate coordination of HL′ through the neutral sulfur atom is given by the variation of ν (C=S), which occurs at 1265 cm^{-1} (for HECD) and at 1275 cm^{-1} (for HCCD) in the free ligands. These bands shift to around 1255 cm^{-1} in the complexes. The non-coordination and neutral nature of the nitrogen is supported by the ν (N–H) value, which occurs around 3140 cm^{-1}. The presence of PPh_3 in all complexes is supported by characteristic bands around 1090 cm^{-1} [ν (P–C)]. The complex $ReOCl_2$ (OEt) (PPh_3) (HCCD) exhibits only one signal that can be assigned to ν (Re–Cl), a fact which suggests that the two chlorides are in equivalent positions, and thus a *trans* configuration for the complex.

Table 3 reports proton NMR chemical shifts of the free ligands and those of the complexes. The free ligands show six distinguishable signals: three multiplets for the methylene protons of the cyclopentene ring, a broad singlet around δ12.35 ppm describing the =S···H—N– intramolecular hydrogen bond, a triplet at δ1.24 ppm for the methyl and a quartet at δ3.46 ppm for the methylene protons of the ethyl group for HECD, and two broad singlets for the methylene protons of the cyclohexyl group in HCCD. When the ligands are coordinated to the rhenium(V), there are very few changes in the spectra. The shifts in the signals for the ligands HL′ are negligible, as one would expect if coordination only occurs through the neutral thiocarbonyl sulfur. The coordinated PPh_3 results in a multiplet around δ7.60 ppm, which corresponds to fifteen protons, in all complexes. The presence of a coordinated ethoxide in *trans*-$ReOCl_2$ (OEt) (PPh_3) (HCCD) is supported by a triplet at δ1.08 ppm and a quartet at δ3.40 ppm. The presence of the solvent of crystallization, acetone, is indicated by a singlet around δ2.10 ppm, which on integration corresponds to six protons.

The question still remains as to why the ligands HECD and HCCD do not tautomerize to the form III in Figure 1, to make available a neutral nitrogen and a negatively charged thiolic sulfur as donor atoms in a bidentate mode of bonding to rhenium. We believe that such tautomerism is prevented by steric, rather than electronic, effects. Steric considerations suggest that the alkyl group on the sp^2-hybridized nitrogen in tautomer III will sterically interact with the methylene protons on the carbon in the 3-position on the cyclopentene ring or with the *cis* ligand (to the nitrogen) if coordination were to occur in a bidentate manner by tautomer III to the metal, giving a (fictitious) complex of possible formulation $ReOCl_2$ (L′) (PPh_3).

Table 3 ^{1}H NMR chemical shift values (δ) in ppm of the compounds in d_6-DMSO at 22°C[a].

Compound	$(CH_2)_4$	$(CH_2)_3$	$(CH_2)_5$	NH	$(CH_2)_{ethyl}$	$(CH_3)_{ethyl}$	S-CH_3	PPh_3	$(CH_2)_{cyclohexyl}$	$(CH_3)_{acetone}$
HECD	1.84(st)	2.73(q)	2.82(q)	12.15(s,br)	3.46(q)	1.24(t)	2.49(d)			
HCCD	1.86(qt)	2.70(q)	2.85(q)	12.55(s,br)			2.49(d)		1.39(s), 1.68(s)	
cis-$ReOCl_3(PPh_3)(HECD)\cdot Me_2CO$	1.84(qt)	2.69(t)	2.81(t)	12.18(s,br)	3.41(q)	1.22(t)	2.47(s)	7.62(m)		2.11(s)
trans-$ReOCl_3(PPh_3)(HECD)\cdot Me_2CO$	1.83(qt)	2.69(t)	2.80(t)	12.16(s,br)	3.43(q)	1.22(t)	2.47(s)	7.63(m)		2.10(s)
cis-$ReOCl_3(PPh_3)(HCCD)\cdot Me_2CO$	1.85(qt)	2.69(t)	2.84(t)	12.45(s)			2.47(s)	7.62(m)	1.39(s), 1.68(s)	2.11(s)
trans-$ReOCl_3(PPh_3)(HCCD)\cdot Me_2CO$	1.84(qt)	2.66(t)	2.81(t)	12.46(s)			2.44(s)	7.59(m)	1.35(s), 1.64(s)	2.08(s)
trans-$ReOCl_2(OEt)(PPh_3)(HCCD)$	1.86(qt)	2.68(t)	2.83(t)	12.47(s)	3.40(q)	1.08(t)	2.46(s)	7.61(m)	1.37(s), 1.66(s)	

[a] st = sextet; q = quartet; s = singlet; br = broad; d = doublet; t = triplet; m = multiplet; qt = quintet.

Table 4 Electronic spectroscopic data for the complexes in nm (ε in $M^{-1}cm^{-1}$)*.

cis-$ReOCl_3$ (PPh_3) (HECD)·Me_2CO	397 (8900)	311 (6600)
trans-$ReOCl_3$ (PPh_3) (HECD)·Me_2CO	396 (13200)	313 (9100)
cis-$ReOCl_3$ (PPh_3) (HCCD)·Me_2CO	395 (21000)	308 (9100)
trans-$ReOCl_3$ (PPh_3) (HCCD)·Me_2CO	396 (25500)	310 (10400)
trans-$ReOCl_2$ (OEt) (PPh_3) (HCCD)	396 (73000)	311 (29800)

* DMF as solvent.

The conversion of *trans*-$ReOCl_3$ (PPh_3) (HECD)·Me_2CO to the *cis* isomer was followed spectrophotometrically at 22°C in acetonitrile and it was found that it is irreversible. The isomerization has a half-life of 41 min, and is independent of the complex concentration. The conversion was complete after 14h, at which time the electronic spectrum was identical to that of *cis*-$ReOCl_3$ (PPh_3) (HECD), prepared by the method given in the Experimental Section, in acetonitrile. In the presence of a twenty-fold mol excess of PPh_3, isomerization was suppressed to the extent that only 5.5% conversion to the *cis* isomer occurred after 20h. Isomerizations of oxorhenium(V) complexes are rare in the literature, although the existence of two isomers of [$ReOCl_3$ $(PEt_2Ph)_2$)] is known.[14]

Monodentate coordination of potentially bidentate N,S^- donor ligands, and of neutral sulfur donor atoms, to oxorhenium(V) have not been observed previously. However, in the exchange reactions of the tetradentate unsaturated N_2S_2 Schiff base ligand *N,N'*-ethylenebis(thioacetylacetonylideneimine) (H_2L) with *trans*-$ReOCl_3$ $(PPh_3)_2$, the neutral complexes ReOCl(L) and (μ–O) [ReO(L)] were isolated.[15] Spectroscopic evidence suggested that coordination to rhenium(V) occurs through the two deprotonated, negatively charged, amido nitrogens and neutral thiocarbonyl sulfur atoms of L^{2-}.

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References

1. B. Bryson, J.C. Dewan, J. Lister-James, A.G. Jones and A. Davison, *Inorg. Chem.*, **27**, 2154 (1988).
2. J. Leonard, D.P. Nowotnik and R.D. Neirinckx, *J. Nucl. Med.*, **27**, 1823 (1986).
3. H.F. Kung, M. Molenar and J. Billings, *J. Nucl. Med.*, **25**, 326 (1984).
4. D.E. Troutner, W.A. Volkert, T.J. Hoffman and R.A. Holmes, *Int. J. Appl. Radiat. Isot.*, **35**, 467 (1984).
5. S.Z. Lever, K.E. Baidoo and A. Mahmood, *Inorg. Chim. Acta*, **176**, 183 (1990).
6. U. Scheffel, H.W. Goldfarb, S.Z. Lever, R.L. Gungon, H.D. Burns and H.N. Wagner Jr., *J. Nucl. Med.*, **29**, 73 (1988).
7. H.F. Kung, Y.-Z. Guo, C.-C. Yu, J. Billings, V. Subramanyam and J.C. Calabree, *J. Nucl. Med.*, **32**, 433 (1989).
8. L.A. Epps, H.J. Burns, S.Z. Lever, H.W. Goldfarb and H.N. Wagner Jr., *J. Appl. Radiat. Isot.*, **38**, 661 (1987).
9. R.C. Walovitch, T.C. Hill, S.T. Garrity, E.H. Cheesman, B.A. Burgess, D.H. O'Leary, A.D. Watson, M.V. Ganey, R.A. Morgan and S.J. Williams, *J. Nucl. Med.*, **30**, 1892 (1989).

10. G. Bandoli, T.I.A. Gerber, J.G.H. du Preez and H.J. Kemp, *Inorg. Chem.*, **32**, 3964 (1993).
11. N.P. Johnson, C.J.L. Lock and G. Wilkinson, *Inorg. Synth.*, **9**, 145 (1967).
12. B. Bordás, P. Sohár, G. Matolocsy and P. Berencsi, *J. Org. Chem.*, **37**, 1727 (1972).
13. J.G.H. du Preez, T.I.A. Gerber and H.J. Kemp, *J. Coord. Chem.*, **25**, 139 (1992).
14. J. Chatt and G.A. Rowe, *J. Chem. Soc.*, 4019 (1962).
15. R. Rossi, A. Marchi, A. Duatti, L. Magon, U. Casselato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 899 (1988).