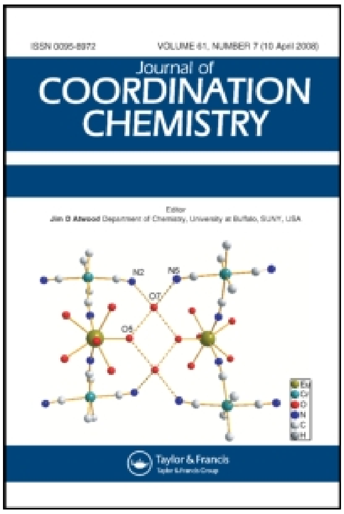

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# COMPLEXES OF RHENIUM(V) AND TECHNETIUM(V) WITH 2-AMINO-1-CYCLOPENTENE-1-DITHIOCARBOXYLIC ACID AND ITS *N*-ALKYL AND *S*-ALKYL DERIVATIVES

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# COMPLEXES OF RHENIUM(V) AND TECHNETIUM(V) WITH 2-AMINO-1-CYCLOPENTENE-1-DITHIOCARBOXYLIC ACID AND ITS *N*-ALKYL AND *S*-ALKYL DERIVATIVES

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The interaction of 2-amino-1-cyclopentene-1-dithiocarboxylic acid, and its *N*-and *S*-alkyl derivatives ($HL_2$), with rhenium(V) and technetium(V) was investigated. Complexes of formula $MOCl(L_2)_2$ (M = Tc, Re) were isolated from the reaction of $(n\text{-}Bu_4N)[MOCl_4]$ with a twofold molar excess of $HL_2$, in acetone, at room temperature. Compounds of type $ReOCl_2(L_2)(PPh_3)$ were characterized with *trans*-$ReOCl_3(PPh_3)_2$ as starting material in ethanol. In all the complexes $L_2^-$ acts as a bidentate $NS^-$-donor ligand. Infrared and $^1H$ n.m.r. data were used to establish the tautomeric forms of the ligands $L_2^-$ in the complexes.

KEYWORDS: technetium(V), rhenium(V), complexes, dithiocarboxylic acids

## INTRODUCTION

A specific goal in recent developments in nuclear medicine has been the design and synthesis of neutral oxotechnetium(V) and rhenium(V) complexes containing $N_2S_2$ 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.[6-10] Up to now, only saturated bis(aminethiol) ligands have been studied extensively.[3-10]

In this study the interaction of 2-amino-1-cyclopentene-1-dithiocarboxylic acid (HACD), and its *N*-alkyl and *S*-alkyl derivatives[11] (Figure 1), with rhenium(V) and technetium(V) was investigated. In principle, the ligands may exist in three tautomeric forms (I-III, Figure 1) in the free uncoordinated form, and they have the potential to coordinate as monodentates (through either N or $S^-$ or S), in a bidentate fashion through either $NS^-$, NS or $SS^-$, or in a terdentate manner (N, $S^-$, S). The reaction of $NS^-$ chelates with *trans*-$ReOCl_3(PPh_3)_2$ and $MOCl_4^-$ (M = Re, Tc) usually lead to the formation of the six-coordinate products

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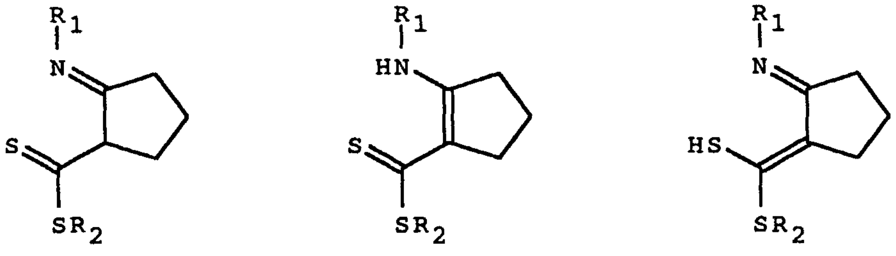


I II III

| $R_1$ | $R_2$ | Abbvn |
|---|---|---|
| H | H | HACD |
| $CH_3$ | H | HMCD |
| $C_2H_5$ | H | HDCD |
| H | $CH_3$ | HNCD |

**Figure 1** The ligands used in this study: 2-Aminocyclopentene-1-dithiocarboxylic acid (HACD) and its derivatives. (HMCD = 2-methylamino-; HDCD = 2-ethylaminocyclopent-1-ene-1-dithiocarboxylic acid; HNCD = methyl-2-aminocyclopent-1-enedithiocarboxylate).

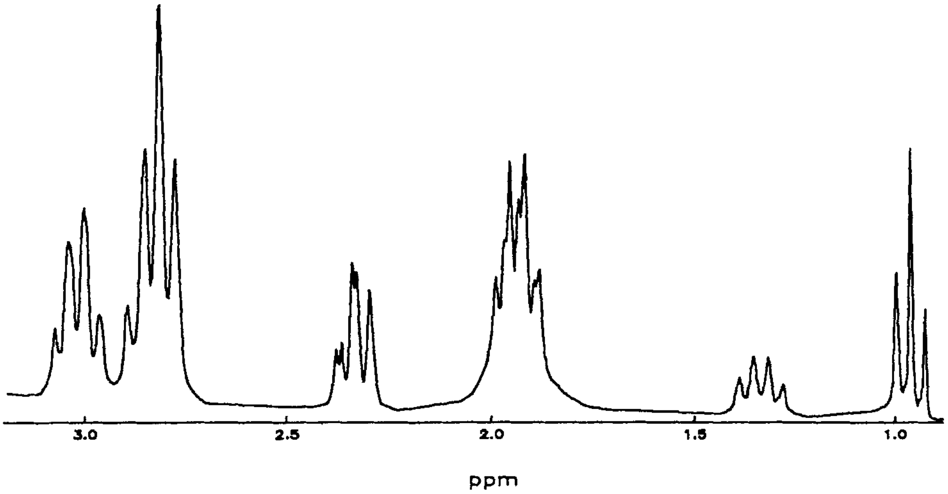


**Figure 2** $^1H$ n.m.r. spectrum of $ReO(OEt)(ACD)_2$ in the region δ0.90–3.40 ppm.

$ReOCl_2(NS)(PPh_3)$[12,13] and $MOCl(NS)_2$,[14] respectively. Products with the formulation $MOCl_2$ (NS) have never been isolated.

## EXPERIMENTAL

### *Health Precautions*

All references to technetium in this paper are to the isotope $^{99}$ Tc, which is a β-emitter (0.292 MeV) with a half-life of 2.12 × $10^5$ years. Normal glassware gives adequate protection against this weak β-emission if the material is handled in milligram amounts. Normal radiation safety produres must be applied at all times, especially with the handling of solid samples, to prevent contamination and inhalation. All operations were carried out with gloves and in a fume hood.

### *Materials*

The compounds $(n\text{-}Bu_4N)[MOCl_4]$ (M = Re, Tc) and *trans*-$ReOCl_3(PPh_3)_2$ were prepared according to literature procedures.[15–16] 2-Amino-1-cyclopentene-1-dithiocarboxylic acid and its derivatives were synthesized by a literature method.[11] All solvents were of analytical grade and were purified and dried by standard methods. All common laboratory chemicals were of analytical grade and were used without further purification.

### *Apparatus*

Scientific instrumentation used in this study is the same as reported elsewhere.[13] Infrared spectra of the complexes were obtained in KBr discs, and $^1$H n.m.r spectra were run in $d_6$-DMSO. Conductivity measurements were made using $10^{-3}$ M solutions of the complexes in acetonitrile. Electronic spectra were all obtained in DMF as solvent, and data are given as $\lambda_{max}$ with extinction coefficients (in the units $M^{-1}$ $cm^{-1}$) in parentheses.

### *Synthesis of the Complexes*

#### $ReOCl(ACD)_2$

To a solution of 102 mg (174 μmol) of $(n\text{-}Bu_4N)[ReOCl_4]$ in 15 $cm^3$ of acetone was added 56 mg (351 μmol) of HACD in 20 $cm^3$ of acetone. After stirring at room temperature for one hour, the orange precipitate that formed was removed by filtration, washed with ethanol and acetone, and dried under vacuum. Recrystallization was from acetonitrile. The yield was 84%, based on Re; mp = 210°C(dec.). Anal; calcd.: C, 26.01; H, 2.91; N, 5.06; Cl, 6.40%. Found: C, 25.87; H,2.95; N, 5.18; Cl, 6.26%. IR: $\nu$(Re=O) 984(s); $\nu$(Re-N) 426(m); $\nu$(NH) 3380(b), 3200(b), 2960(b); $\delta(NH_2)$ 1618(m); $\nu$(C=C) 1520(s); $\nu$(Re-S) 362(m); $\nu$(Re-Cl) 318(m); $\nu_{asym}$(CSS) 887.3(m), 868.0(m) $cm^{-1}$. $^1$H n.m.r.: $\delta$1.95(q,4H,$^4CH_2$); 2.86(t,4H,$^3CH_2$); 3.03(t,4H,$^5CH_2$); 9.98(s,2H,N$H$); 11.70(s,2H,N$H$) ppm. Electronic spectrum: 384(14000), 336(12900), 312sh. Conductivity: 57 $ohm^{-1}$ $cm^2$ $mol^{-1}$.

### $\mathrm{ReO(OEt)(ACD)_2}$

This complex was obtained as a green precipitate after stirring a mixture of 100 mg of $(n\text{-}\mathrm{Bu_4N})[\mathrm{ReOCl_4}]$ and 55 mg of HACD in 30 $\mathrm{cm^3}$ of ethanol for an hour at room temperature. Recrystallization from acetonitrile led to decomposition of the compound. Yield = 73%; mp = 172°C(dec.). Anal; calcd.: C, 29.83; H, 3.75; N, 4.97%. Found: C, 29.39; H, 3.97; N, 5.25%. IR: $\nu$(Re=O) 978(s); $\nu$(Re–N) 439(m); $\nu$(NH) 3350(b), 3150(b), 2950(b); $\delta(\mathrm{NH_2})$ 1626(m); $\nu$(C=C) 1495(s,b); $\nu$(Re–S) 352(m); $\nu_{\mathrm{asym}}$ (CSS) 875(w), 864(w) $\mathrm{cm^{-1}}$. $^1$H n.m.r.:$\delta$1.92(q,4H,$^4\mathrm{C}H_2$); 2.80(t,4H,$^3\mathrm{C}H_2$); 2.99(t,4H,$^5\mathrm{C}H_2$); 9.88(s,2H,N*H*); 11.63(s,2H,N*H*); 3.18(qt,2H,$\mathrm{OC}H_2\mathrm{CH_3}$); 0.96(t,2H,$\mathrm{OCH_2C}H_3$) ppm. Electronic spectrum: 383(11400), 360(12700), 335(13200). Conductivity: 61 $\mathrm{ohm^{-1}\ cm^2mol^{-1}}$.

### $\mathrm{ReOCl_2(ACD)(PPh_3)}$

To 100 mg (120 μmol) of *trans*-$\mathrm{ReOCl_3(PPh_3)_2}$ in 15 $\mathrm{cm^3}$ of ethanol was added 41 mg (258 μmol) of HACD in 10 $\mathrm{cm^3}$ of ethanol. The reaction mixture was stirred at room temperature for an hour, during which time a brick red, crystalline powder precipitated continuously. The material was collected by filtration, washed with benzene, diethyl ether and ethanol, and dried under vacuum. Recrystallization was from acetone/ethanol to give a yield of 79%, based on Re; mp = 184°C(dec). Anal; calcd.: C, 41.56; H, 3.34; N, 2.02; Cl, 10.22%. Found: C, 42.03; H, 3.55; N, 1.46; Cl, 10.57%. IR: $\nu$(Re=O) 976(s); $\nu$(Re–N) 442(w); $\nu$(NH) 3400(b), 3150(b), 2970(b); $\delta(\mathrm{NH_2})$ 1618(m); $\nu$(C=C) 1522(s); $\nu$(Re–S) 353(m); $\nu$(Re–Cl) 315(w), 286(m); $\nu$(P–C) 1094(m); $\nu_{\mathrm{asym}}$ (CSS) 883(w), 871(w) $\mathrm{cm^{-1}}$. $^1$H n.m.r.: $\delta$1.87(q, 2H,$^4\mathrm{C}H_2$); 2.82(t,2H,$^3\mathrm{C}H_2$); 3.05(t,2H,$^5\mathrm{C}H_2$); 8.05(s,1H,N*H*); 9.13(s,1H,N*H*); 7.66(m,15H,$\mathrm{P}Ph_3$) ppm. Electronic spectrum: 383(10600), 332(12500). Conductivity: 68 $\mathrm{ohm^{-1}\ cm^2\ mol^{-1}}$.

### $\mathrm{TcOCl(ACD)_2}$

This complex was isolated as a brick red powder from the reaction of 100 mg (200 μmol) of $(n\text{-}\mathrm{Bu_4N})[\mathrm{TcOCl_4}]$ with 65 mg of HACD in 30 $\mathrm{cm^3}$ of acetone at room temperature. Recrystallization from acetonitrile gave orange-red microcrystals in a yield of 76%, based on Tc; mp = 109°C (dec.). Anal; calcd.: C, 30.87; H, 3.45; N, 6.00; Cl, 7.59%. Found: C, 30.72; H, 3.22; N,5.33; Cl, 7.63%. IR: $\nu$(Tc=O) 964(s); $\nu$(Tc–N) 428(m); $\nu$(Tc-S) 386(m); $\nu$(Tc-Cl) 287(w); $\nu$(NH) 3400(b), 3200(b), 2950(b); $\delta(\mathrm{NH_2})$ 1618(m); $\nu$(C=C) 1504(s); $\nu_{\mathrm{asym}}$(CSS) 855(w), 869(w) $\mathrm{cm^{-1}}$. $^1$H n.m.r.: $\delta$1.95(q,4H,$^4\mathrm{C}H_2$); 2.80(t,4H,$^3\mathrm{C}H_2$); 3.01(q,4H,$^5\mathrm{C}H_2$); 10.11(s,2H,N*H*); 11.69(s,2H,N*H*) ppm. Electronic spectrum: 379(31500), 283(21000). Conductivity: 74 $\mathrm{ohm^{-1}\ cm^2mol^{-1}}$.

### $[\mathrm{MOCl(L_2)_2}]$(M = Re, Tc; $\mathrm{HL_2}$ = HMCD, HDCD, HNCD)

The syntheses of these complexes were effected by following the same procedure. About 200 μmol of $(n\text{-}\mathrm{Bu_4N})[\mathrm{MOCl_4}]$ was stirred with at least a twofold molar excess of the ligands $HL_2$ in about 30 cm$^3$ of acetone at room temperature for an hour. In every case an orange/brick red precipitate formed, and which was collected by filtration, washed with ethanol and acetone, and dried under vacuum. The yields varied between 76 and 82%.

$ReOCl(MCD)_2$

Anal; calcd.: C, 28.88; H, 3.46; N, 4.81; Cl, 6.09%. Found: C, 28.89; H, 3.72; N, 4.73; Cl, 6.69%. Mp = 209°C(dec.). IR: $\nu$(Re=O) 976(s); $\nu$(NH) 3412(b), 3000(b); $\nu_{asym}$ (CSS) 882(w), 868(w); $\nu$(Re–N) 446(m); $\nu$(Re–S) 349(m); $\nu$(Re–Cl) 302(m) cm$^{-1}$. $^1$H n.m.r.: $\delta$1.96(q,4H,$^4$C$H_2$); 2.87(t,4H,$^3$C$H_2$); 3.11(t,4H,$^5$C$H_2$); 10.50(s,2H,N$H$); 3.35(s,6H,C$H_3$) ppm. Electronic spectrum: 408(47600), 389sh, 314sh, 283(13600). Conductivity: 51 ohm$^{-1}$ cm$^2$mol$^{-1}$.

$TcOCl(MCD)_2$

Anal; calcd.: C, 33.97; H, 4.07; N, 5.66; Cl, 7.16%. Found: C, 34.05; H, 4.58; N, 5.58; Cl, 6.98%. Mp = 156°C(dec.). IR:$\nu$(Tc=O) 961(s); $\nu$(NH) 3340(b), 3040(b); $\nu_{asym}$ (CSS) 884(w), 872(w); $\nu$(Re–N) 436(m); $\nu$(Re–S) 383(m); $\nu$(Re–Cl) 281(m) cm$^{-1}$. $^1$H n.m.r.: $\delta$1.99(q,4H,$^4$C$H_2$); 2.88(t,4H,$^3$C$H_2$); 3.10(t,4H,$^5$C$H_2$); 10.55(s,2H,N$H$); 3.34(s,6H,C$H_3$) ppm. Electronic spectrum: 379(14700), 309(9800), 277(21000). Conductivity: 67 ohm$^{-1}$ cm$^2$mol$^{-1}$.

$ReOCl(DCD)_2$

Anal; calcd.: C, 31.49; H, 3.96; N, 4.59; Cl, 5.81%. Found: C, 31.25; H, 4.17; N, 4.46; Cl, 6.09%. Mp = 118°C(dec.). IR: $\nu$(Re=O) 976(s); $\nu$(NH) 3360(b), 2935(b); $\nu_{asym}$ (CSS) 870(w), 880(w); $\nu$(Re–N) 447(m); $\nu$(Re–S) 360(m); $\nu$(Re–Cl) 303(m) cm$^{-1}$. $^1$H n.m.r.: $\delta$1.98(q,4H,$^4$C$H_2$); 2.87(t,4H,$^3$C$H_2$); 3.16(t,4H,$^5$C$H_2$); 10.52(s,2H,N$H$); 1.31(t,6H,C$H_3$); 3.72(qt,4H,C$H_2^{Et}$) ppm. Electronic spectrum: 360(24300), 304sh, 278(21700). Conductivity: 63 ohm$^{-1}$ cm$^2$mol$^{-1}$.

$ReOCl(NCD)_2$

Anal; calcd.: C, 28.88; H, 3.46; N, 4.81; Cl, 6.09%. Found: C, 28.73; H, 3.75; N, 4.70; Cl, 6.11%. Mp = 199°C(dec.). IR: $\nu$(Re=O) 990(vs); $\nu$(Re–N) 444(m); $\nu$(Re–S) 376(m); $\nu$(C=NH) 1588 cm$^{-1}$; $\nu$(Re–Cl) could not be assigned with certainty. $^1$H n.m.r.: $\delta$1.95(q,4H,$^4$C$H_2$); 3.00(t,4H,$^3$C$H_2$); 3.05(t,4H,$^5$C$H_2$); 13.85(s,2H,N$H$); 2.83(s,6H,C$H_3$) ppm. Electronic spectrum: 384(15000), 339(10400), 313(12000), 277(15700). Conductivity: 44 ohm$^{-1}$ cm$^2$mol$^{-1}$.

$TcOCl(NCD)_2$

Anal; calcd.: C, 33.97; H, 4.07; N, 5.66; Cl, 7.16%. Found: C, 33.18; H, 4.12; N, 5.82; Cl, 7.33%. Mp = 196°C(dec.). IR: $\nu$(Re=O) 968(vs); $\nu$(Tc–N) 455(m); $\nu$(Tc–S) 374(m); $\nu$(C=NH) 1579(m); $\nu$(Tc–Cl) 316(m) cm$^{-1}$. $^1$H n.m.r.: $\delta$2.03(q,4H,$^4$C$H_2$); 2.95(t,4H,$^3$C$H_2$); 3.11(t,4H,$^5$C$H_2$); 12.52(s,2H,N$H$); 2.87(s,6H,C$H_3$) ppm. Electronic spectrum: 385(12800), 308(10900), 277(19300). Conductivity: 49 ohm$^{-1}$ cm$^2$mol$^{-1}$.

### [ReOCl$_2$(L$_2$)(PPh$_3$)]

These complexes were prepared by heating under reflux a mixture of 200 μmol of *trans*-ReOCl$_3$ (PPh$_3$)$_2$ and an equimolar quantity of the ligand HL$_2$ in 30 cm$^3$ of ethanol for 30 min. After cooling to room temperature, the solution was filtered to give crystalline solids, which were washed with ethanol and acetone, and recrystallized from acetonitrile.

### ReOCl$_2$(MCD)(PPh$_3$)

Anal; calcd.: C, 42.43; H, 3.56; N, 1.98; Cl, 10.02%. Found: C, 42.76; H, 3.85; N, 1.50; Cl, 9.91%. Colour: green. Mp = 142°C(dec.). Yield: 81%. IR: $\nu$(Re=O) 970(s); $\nu$(NH) 3350(b), 3010(b) ; $\nu_{asym}$ (CSS) could not be assigned with certainty; $\nu$(Re–N) 443(m); $\nu$(Re–S) 347(m); $\nu$(Re–Cl) 318(m), 307(m); $\nu$(P–C) 1092(s) cm$^{-1}$. $^1$H n.m.r.: $\delta$1.95(q,2H,$^4$C$H_2$); 2.86(t,2H,$^3$C$H_2$); 3.10(t,2H,$^5$C$H_2$); 10.48(s,1H,N$H$); 7.60(m,15H,P$Ph_3$); 3.34(s,3H,C$H_3$) ppm. Electronic spectrum: 428(22000), 389sh, 310sh, 272(10800). Conductivity: 48 ohm$^{-1}$ cm$^2$mol$^{-1}$.

### ReOCl$_2$(DCD)(PPh$_3$)

Anal; calcd.: C, 43.27; H, 3.77; N, 1.94; Cl, 9.82%. Found: C, 43.26; H, 3.51; N, 1.61; Cl, 10.11%. Colour: green. Mp = 190°C. Yield: 72%. IR: $\nu$(Re=O) 972(s); $\nu$(NH) 3260(b), 2880(b) ; $\nu_{asym}$ (CSS) 870(w), 873(w); $\nu$(Re–N) 457(m); $\nu$(Re–S), $\nu$(Re–Cl) could not be assigned with certainty; $\nu$(P–C) 1091(s) cm$^{-1}$. $^1$H n.m.r.: $\delta$1.94(q,2H,$^4$C$H_2$); 2.84(t,2H,$^3$C$H_2$); 3.13(t,2H,$^5$C$H_2$); 10.36(s,1H,N$H$); 7.63 (m,15H,P$Ph_3$); 1.29(t,3H,C$H_3$); 3.70(qt,2H,C$H_2{}^{Et}$) ppm. Electronic spectrum: 354(34600), 307sh, 274sh. Conductivity: 46 ohm$^{-1}$ cm$^2$mol$^{-1}$.

### ReOCl$_2$(NCD)(PPh$_3$)

Anal; calcd.: C, 42.43; H, 3.56; N, 1.98; Cl, 10.02%. Found: C, 42.39; H, 3.60; N, 2.20; Cl, 10.15%. Colour: maroon.Mp = 178°C. Yield: 82%. IR: $\nu$(Re=O) 963(s); $\nu$(Re–N) 446(m), $\nu$(Re–S) 363(m); $\nu$(Re–Cl) uncertain; $\nu$(C=NH) 1622(m); $\nu$(P–C) 1094(s) cm$^{-1}$. $^1$H n.m.r.: $\delta$1.93(q,2H,$^4$C$H_2$); 2.99(t,2H,$^3$C$H_2$); 3.08(t,2H,$^5$C$H_2$); 13.26(s,1H,N$H$); 7.41(m,15H,P$Ph_3$); 2.83(s,3H,C$H_3$) ppm. Electronic spectrum: 384(12700), 313(10300), 273(16200). Conductivity: 68 ohm$^{-1}$ cm$^2$mol$^{-1}$.

## RESULTS AND DISCUSSION

The complexes of formulation MOCl(L$_2$)$_2$ (M=Re, Tc) were prepared by the simple ligand substitution of ($n$-Bu$_4$N)[MOCl$_4$] by a molar excess of HL$_2$ in acetone at room temperature under aerobic conditions. All efforts to prepare and isolate species of formulae MOCl$_2$(ACD) or MOCl$_3$(ACD), by using equimolar quantities of reactants, were unsuccessful , and led to the formation of impure products. The rhenium complexes could also be prepared by the reaction of *trans*-ReOCl$_3$(PPh$_3$)$_2$ with at least a twofold molar excess of HL$_2$ under reflux conditions in acetone, but this method of synthesis led to a lower yield and more drastic manipulations to obtain a pure product. However, in ethanol the products ReOCl$_2$(L$_2$)(PPh$_3$) and

$ReO(L_2)_2$ (OEt) could be isolated by the reactions of *trans*-$ReOCl_3(PPh_3)_2$ and ($n$-$Bu_4N$)[$ReOCl_4$], respectively, with $HL_2$.

All the compounds are insoluble in common organic solvents, but they are fairly soluble in acetonitrile and DMF. Conductivity measurements in DMF indicate that the complexes are uncharged; upon standing, however, the conductivity slowly increases, probably due to halide ion dissociation. Attempts to isolate the solvolysis products yielded dark oils that could not be induced to crystallize. All the compounds are diamagnetic in solution, which is in agreement with previous work on metallate(V) species in a distorted octahedral milieu.[17]

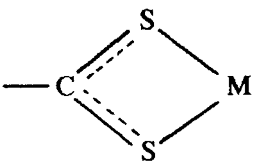
## *Characterization*

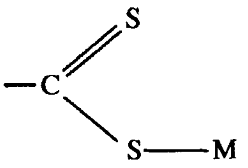
### Complexes with HACD, HMCD, HDCD

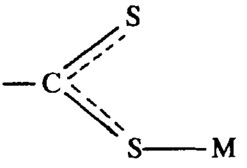
Infrared data were compiled by comparing the spectra of the metal complexes with those of dithiocarbazates,[18,19] dithiocarboxylates[20] and dithiocarbamates.[21] It is evident that bonding of $L_2^-$ to the metals has taken place either through N,$S^-$ or S,$S^-$ donor atoms, since the bands around 2550 $cm^{-1}$ in free $HL_2$, due to $\nu$(S-H), are missing in the complexes.

Three bands appear in the region 2800–3400 $cm^{-1}$ in all $ACD^-$ complexes, indicating that these are due to $NH_2$ stretching instead of NH stretching, and that coordination also occurs through the amino group (uncoordinated primary amines usually show two bands as against one for imines in the range 3500–3400 $cm^{-1}$). The $NH_2$ bending mode of vibration which is little affected due to chelation, remain basically unaltered in the complexes (at 1616 $cm^{-1}$ in free HACD and around 1618 $cm^{-1}$ in the complexes). A medium intensity band at 1319 $cm^{-1}$ in the free ligand and around 1340 $cm^{-1}$ in the complexes appears to be due to a combination of $\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{N})$ and $\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{S})$, and doublets at about 1288 $cm^{-1}$ in the complexes (at 1291 $cm^{-1}$ in free HACD) are possibly due to mixing of $\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{S})$ and $\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{N})$. Two bands in the region 2880–3420 $cm^{-1}$ in the complexes with $MCD^-$ and $DCD^-$ as ligands are assigned to the NH stretching frequency, and this shows that coordination also occurs through the secondary amines (uncoordinated secondary amines usually show one band).

In the case of dithiocarboxylate metal complexes, bonding may occur in any of the following ways:

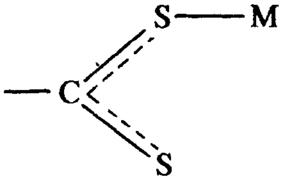






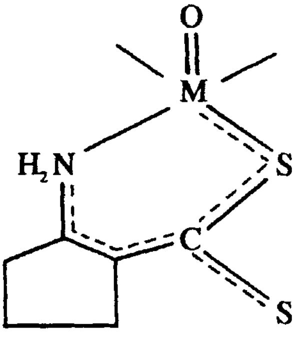
The question regarding the nature of sulfur chelation may be settled in the light of the following observations.

In dithiocarbamates, where asymmetric CSS stretching is observed[22] at *ca* 1000 $cm^{-1}$, in the case of disulfur chelation a single band is usually observed, whereas for unidentate sulfur coordination, this band is split. This criterion found successful application in distinguishing the types of sulfur bonding in metal dithiocarbazates.[23] In the case of vanadium(IV) complexes of aryl dithiocarboxylates, which involve disulfur chelation, the band in the region of 1020 $cm^{-1}$ was attributed to $\nu_{asym}$ (CSS) and a band at 950 $cm^{-1}$ to $\nu_{sym}$ (CSS).[24] On the other hand, in studies with aryl dithiocarboxylic acid complexes and some of their sulfur addition products, the bands in the range 1035 to 900 $cm^{-1}$ were assigned to C=S and other modes of CS stretching frequencies.[20] While no band in the region of 1000 $cm^{-1}$ is observed in either free $HL_2$ or the complexes, a strong band at 878 $cm^{-1}$ in the free HACD (and around 875 $cm^{-1}$ in other ligands $HL_2$) is symmetrically bifurcated in the complexes (*e.g.*, at 887 and 868 $cm^{-1}$ in $ReOCl(ACD)_2$). This phenomenon is attributed to $\nu_{asym}$ (CSS), and the formation of two bands in the chelates may be inferred due to unidentate sulfur bonding in them. A band at 610 $cm^{-1}$ in free HACD is displaced to a higher fequency around 620 $cm^{-1}$ in the complexes, and it is tentatively assigned to either $\nu_{sym}$ (CSS) or to $\nu$(C-S). The displacement of this band to higher energy is interpreted as due to presence of the following unit.



Medium intensity bands in the region 426–460 $cm^{-1}$ in the complexes are ascribed to M-N stretching, and new bands in the range 345–386 $cm^{-1}$ seem to be due to M-S stretching. The $\nu$(Re=O) mode occurs in the narrow range of 976–984 $cm^{-1}$ as a high intensity band. These values are in the range that was previously found for monooxorhenium(V) complexes in an octahedral environment.[17,25] Complexes with a chloride in the *trans* position to the rhenyl oxo group in neutral distorted octahedra have the Re=O stretch in the 970–990 $cm^{-1}$ region.[11,26,27] The $\nu$(Tc=O) mode of $TcOCl(ACD)_2$ occurs at 964 $cm^{-1}$, which is 20 $cm^{-1}$ lower than in the rhenium analogue. An average difference of 20 $cm^{-1}$ for $\nu$(M=O) in similar technetium(V) and rhenium(V) complexes has been found previously.[26,28]

The nature of bonding in the complexes thus appears to be as shown below.



No definite conclusions could be made regarding the relative positions of the coordinating atoms in the complexes, *i.e.*, whether the $ACD^-$ ligands in the complexes $[MOX(L_2)_2]$ (M=Re, Tc; X=Cl, OEt) have a mutual *cis* or *trans* configuration. However, since the negatively charged deprotonated sulfur is a good σ-donor and a good π-acceptor and the amine nitrogen is a good σ-donor, one would expect these two donor atoms of two different $L_2^-$ molecules to occupy *trans* positions relative to each other in the complexes, *i.e.*, the ligands $L_2^-$ will be in positions *cis* to each other, as was previously found in similar examples involving technetium(V).[29]

The chemical shifts obtained from $^1H$ n.m.r. spectra clearly show that the two amino hydrogens of the free ligand HACD (singlets at δ9.30 and 10.99 ppm) in $d_6$-DMSO are non-equivalent, which suggests tautomer II (in Figure 1) for the free ligand. As expected, due to metal-amino group bonding, the $NH_2$ protons' resonances suffer a downfield shift, except for the complex $ReOCl_2(ACD)(PPh_3)$, where an upfield shift is observed and the two protons are somewhat shielded. In all the complexes with $MCD^-$ and $DCD^-$, the nitrogen donor atoms of the chelates remain protonated, and the alkyl groups on the nitrogens are observed as a singlet for $CH_3$ (for $MCD^-$) and as a quartet (qt) and triplet for the ethyl group of $DCD^-$. All the methylene protons are affected by chelation and suffer downfiled shifts. The shifts for protons $^4CH_2$ and $^3CH_3$ are of the order of about 0.20 ppm, while the $^5CH_2$ protons experience a shift of about 0.30 ppm. The presence of a coordinated ethoxide in the complex $ReO(ACD)_2(OEt)$ is indicated by a triplet (at δ0.96 ppm) and a quartet (at δ3.18 ppm), which correspond to the methyl and methylene protons of $OCH_2CH_3$, respectively. The electronic spectra of these complexes in DMF solution have two absorption maxima in the range 280–390 nm. Both bands are due to internal ligand transitions which occur in the range 300–400 nm for HACD.

It was previously found that the ligand HACD forms complexes with the transition metals Ni(II),[30] Pt(II),[30] Pd(II),[30] Mo(VI),[31] and V(IV).[32] Crystallographic evidence, however, is not available. It was suggested[30] that in $ACD^-$ complexes with Ni(II), Pt(II) and Pd(II), coordination occurs through the amino nitrogen and the deprotonated thiolic sulfur atoms. It is believed[31,32] that the complexes $MoOX_2(ACD)_2$ and $V(ACD)_4$ are monomeric neutral species with $S,S^-$ rather than $N,S^-$ bonding by $ACD^-$.

In the literature, only one example where HDCD has been used as a ligand was found.[33] The compound $Bi(DCD)_3$ was isolated, in which coordination by $DCD^-$ occurs as a bidendate through the $CS_2^-$ -group. No metal complexes of HMCD are known.

## Complexes with $HL_2$ = HNCD

In the free state, the ligand HNCD has no band in the infrared spectrum which can be ascribed to ν(S—H). The presence of three bands in the range 2800–3400 $cm^{-1}$ and the presence of the C=S entity is indicated by a strong absorption at 1312 $cm^{-1}$ [ν(C=S)].

In addition to the expected signals for the methylene protons of free, uncoordinated HNCD, the $^1H$ n.m.r. spectrum also contains two separate signals for the amine protons. One of these singlets is shifted considerably downfield to δ10.87 ppm, which is characteristic and typical for chelates in which intramolecular hydrogen bonding exists. The other signal appears in the range that would normally be expected for an amine hydrogen. The S-$CH_3$ methyl group appears as a singlet at δ2.48 ppm. The tautomeric structure II in Figure 1 for HNCD can thus be elucidated from the spectroscopic data.

In the infrared spectra of the complexes, only one band is observed (around 3400 $cm^{-1}$) in the range 2800–3400 $cm^{-1}$ [$\nu$(N–H)], which illustrates the presence of a coordinated imine nitrogen. An additional band in the range 1579–1622 $cm^{-1}$ is assigned to the presence of a coordinated C=NH group. A medium intensity band around 1540 $cm^{-1}$ in the complexes $MOCl(NCD)_2$ appears to be due to $\nu$(C=C), while others around 450 and 370 $cm^{-1}$ are due to $\nu$(M–N) and $\nu$(M–S), respectively.

$^1$H n.m.r spectra of the complexes are characterized by a single signal which appears somewhat downfield at about δ13 ppm, and which is assigned to the N*H* proton. All other signals appear further downfield than do the corresponding protons of the free ligand. The spectroscopic data thus suggest that the ligand $NCD^-$ exists in tautomeric form III (Figure 1) in the complexes. In this manner the chelate acts as a uninegative bidentate ligand, as is required for the formulations $MOCl(NCD)_2$ and $ReOCl_2(NCD)(PPh_3)$.

Only one study on the coordination properties of methyl-2-amino-1-cyclopentenedithiocarboxylate ($NCD^-$) could be found in the literature.[34] Bis-bidentate complexes of Ni(II), Pd(II) and Pt(II) of $NCD^-$ were prepared, and X-ray crystal analyses have shown that chelation occurs through a thioketonate sulfur and the imine nitrogen, in the same way as suggested for the complexes in this study. *Trans* planar coordination of the chelates was found in $Ni(NCD)_2$, while in the Pt(II) and Pd(II) derivatives the two ligands coordinate in a *cis*-planar configuration, due to the presence of a water molecule that is hydrogen bonded to the imine protons.

Information on rhenium(V) and technetium(V) complexes with uninegative bidentate nitrogen-sulfur donor ligands is limited in the literature. A crystal structure study[12] of $[ReOCl_2\{p\text{-}MeC_6H_4N{=}C(OEt)\text{-}S\}(PPh_3)]$ has shown that the N,S-donor ligand coordinates in the equatorial plane *cis* to the oxo group, with the neutral nitrogen in the position *trans* to the phosphorus atom, and a chloride *trans* to the oxo oxygen. This particular configuration can be explained by the *trans* influence, in which the good σ-donor nitrogen occupies the position *trans* to the good π-acceptor ligand $PPh_3$.

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