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Bis-Cyclopentadienyl(Methylcyclopentadienyl)N,N-Dialkyldithiocarbamato Chloro Zirconium(IV) Compounds

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Zirconium(IV) N,N-dialkyldithiocarbamates of the type $Cp_2Zr(S_2CNR_2)Cl$ *and* $(MeCp)_2Zr(S_2CNR_2)Cl$ *(R = Me, Et) have been prepared by reaction of dicyclopentadienyl zirconium(IV) dichloride and bismethylcyclopentadienyl zirconium(IV) dichloride with anhydrous sodium N,N-dialkyldithiocarbamates in refluxing dichloromethane. Molecular weight, conductance and infrared data demonstrate that these complexes are monomeric nonelectrolytes in which the dithiocarbamate ligands are bidentate. Therefore, the zirconium(IV) atom may be assigned a coordination number 5. Proton nmr studies have also been carried out for these complexes.*

Introduction

The dithiocarbamate ligands by virtue of their (i) low charge, and (ii) relatively small 'bites' (2.8–2.9 Å) are particularly well suited for the stabilisation of higher coordination states of metals. Thus many high coordination state dithiocarbamate complexes such as $Ti(S_2CNR_2)_3Cl$ [1, 2], $VO[S_2CN(C_2H_5)_3]_3$ [3], $NbO[S_2CN(C_2H_5)_2]_3$ [3], $Mo(NO)[S_2CN(n\text{-}C_4H_9)_2]_3$ [4] and $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ [5] have been reported.

The present communication deals with the preparation and characterisation of complexes of the type $Cp_2Zr(S_2CNR_2)Cl$ and $(MeCp)_2Zr(S_2CNR_2)Cl$ (R = Me, Et).

Experimental

Reagents and Techniques

Sodium salts of dithiocarbamic acid, $Na(S_2CNR_2)$, were prepared by the method [6] described by Klopping and Kerk. The above sodium salts were dried under vacuum over phosphorus pentoxide (first at room temperature and then at 110 °C). Dicyclopentadienyl zirconium(IV) dichloride was prepared by reaction of zirconium tetrachloride with sodium salt of cyclopentadiene in tetrahydrofuran [7]. Bismethylcyclopentadienyl zirconium(IV) dichloride was prepared by reaction of zirconium tetrachloride with sodium salt of methylcyclopentadiene in tetrahydrofuran [8].

Dichloromethane was dried by refluxing for 24 hours over calcium hydride. Nitrobenzene was purified for conductance measurements by the method described by Fay *et al.* [9].

Preparation of the Complexes

The dicyclopentadienyl zirconium(IV) dichloride and bismethylcyclopentadienyl zirconium(IV) dichloride were refluxed separately in 100 ml of dichloromethane with stoichiometric amounts of anhydrous sodium salts of the N,N-dialkyldithiocarbamates for 24 hours. The solution was then filtered and the volume of the filtrate was reduced to ~25 ml. Colourless crystals of the compounds were obtained by adding petroleum ether (60–80 °C) (~15 ml) to the above concentrated filtrate and allowing the mixture to stand overnight.

Bis-cyclopentadienyl N,N-dimethyldithiocarbamato chlorozirconium(IV): This complex was prepared in refluxing dichloromethane by reaction of 0.2922 g (0.001 mol) of dicyclopentadienyl zirconium(IV) chloride and 0.143 g (0.001 mol) of sodium N,N-dimethyldithiocarbamate, $Na(S_2CNMe_2)$; yield 0.298 g (79%).

Bis-cyclopentadienyl N,N-diethyldithiocarbamato chloro zirconium(IV): This complex was prepared in refluxing dichloromethane by reaction of 0.2922 g (0.001 mol) of dicyclopentadienyl zirconium(IV) dichloride and 0.171 g (0.001 mol) of N,N-diethyl dithiocarbamate, $Na(S_2CNEt_2)$; yield 0.291 g (72%).

Bis-methylcyclopentadienyl N,N-diethyldithiocarbamato chloro zirconium(IV): This complex was prepared in refluxing dichloromethane by reaction of 0.3202 g (0.001 mol) of bis-methylcyclopentiadienyl zirconium(IV) dichloride and 0.143 g (0.001 mol) of $Na(S_2CNMe_2)$; yield 0.283 g (70%).

Bis-methylcyclopentadienyl N,N-diethyldithiocarbamato chloro zirconium(IV): This complex was prepared in refluxing dichloromethane by reaction of 0.3202 g (0.001 mol) of bis-methylcyclopentadienyl zirconium(IV) dichloride and 0.171 g (0.001 mol) of $Na(S_2CNEt_2)$; yield 0.273 g (63%).

Table I lists the important physical characteristics of the complexes.

TABLE I. Yields and Physical Characteristics (Λ in $\text{Ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$)

Compound	Molecular wt.		M.P.	Conductance data		Found (%)					Calculated (%)				
	Found	Calcd.	(°C)	Molarity × 10^3	Λ	C	H	N	Zr	Cl	C	H	N	Zr	Cl
$Cp_2Zr(S_2CNMe_2)Cl$	350	376.7	205–210(d)	0.5	0.55	40.2	4.4	4.0	23.1	9.2	41.4	4.3	3.7	24.2	9.4
$Cp_2Zr(S_2CNEt_2)Cl$	355	404.7	172–175(d)	0.5	0.59	43.2	5.0	3.4	24.0	8.5	44.5	4.9	3.5	22.5	8.8
$(MeCp)_2Zr(S_2CNMe_2)Cl$	395	404.7	145–148 (d)	0.5	0.42	44.8	4.9	3.6	22.8	8.6	44.5	4.9	3.5	22.5	8.8
$(MeCp)_2Zr(S_2CNEt_2)Cl$	369	432.7	147–151 (d)	0.5	0.46	46.8	5.3	3.4	20.5	8.0	47.1	5.6	3.2	21.1	8.2

Molecular Weight and Conductance Measurements

Molecular weights were determined ebullioscopically in benzene using a Gallen Kamp (U.K.) ebulliometer.

Conductance measurements were made in nitrobenzene at 30 ± 05 °C with a Beckmann Conductivity Bridge Model No. RC-18A.

Infrared Spectra

Infrared spectra were recorded in solid state (KBr pellets) in the region 4000–250 cm^{-1} with a Perkin Elmer 621 grating spectrophotometer.

Nuclear Magnetic Resonance Spectra

The proton nmr spectra were recorded at ambient temperature (30 °C) at sweep width of 500 Hz with a Varian A-60 spectrometer. Spectra were recorded in triplicate, and the values given in Table II are average values; the magnetic field sweep was calibrated with a standard sample of chloroform and tetramethylsilane (1%) in deuterated chloroform.

Results and Discussion

The methods used for preparation and isolation of the compounds give materials of good purity as judged by satisfactory elemental analyses and by proton nmr spectra of deuterichloroform solutions (Table II). All the four compounds are new.

All the above complexes crystallise as colourless crystals. They are soluble, in carbon disulfide, benzene, dichloromethane and chloroform. These complexes are thermally stable but decompose near their melting points. The solids are quite stable in air but their solutions are hydrolysed relatively rapidly.

Conductance measurements (Table I) show that all the four complexes are essentially nonelectrolytes in nitrobenzene. Molecular weight data are presented in Table I. All of the complexes are soluble enough to be studied and are monomeric in benzene solution.

The chief interest in the preparation of these complexes is the attachment of dithiocarbamate ligand. A coordination number of 5 may be assigned if the dithiocarbamate ligands behave as bidentate as in $Mo(NO)(S_2CNR_2)_3$ (R = Me [10] or n-Bu [4]); however, the coordination number of 4 would result if the dithiocarbamate ligands behave as an s-bonded monodentate ligand, as in $Ru(NO)(S_2CNR_2)_3$ (R = Me [10] or Et [11]). The two bonding possibilities can be distinguished by infrared spectroscopy since complexes having monodentate dithiocarbamate ligands exhibit additional infrared bands not found for complexes having only bidentate ligands [11–17].

Table III lists the characteristic infrared frequencies for $Cp_2Zr(S_2CNR_2)Cl$ and $(MeCp)_2Zr(S_2CNR_2)$-Cl (R = Me, Et) complexes. Some of the infrared

TABLE II. Proton Chemical Shift (in Hz) and Coupling Constant Data (in Hz) at 30 °C.[a]

Compound	Deuterichloroform Solution				J
	π-C_5H_5/C_5H_4	CH_3 of π-$CH_3C_5H_4$	$-CH_2-$	$-CH_3$ of $[S_2CNR_2]$	
$Cp_2Zr(S_2CNMe_2)Cl$	−369.7	–	–	−200.7	–
$Cp_2Zr(S_2CNEt_2)Cl$	−368.8	–	−230.8 q	−76.2 t	7.1
$(MeCp)_2Zr(S_2CNMe_2)Cl$	−355.6	−129.4	–	−201.4	–
$(MeCp)_2Zr(S_2CNEt_2)Cl$	−355.2	−129.5	−231.4 q	−76.6 t	7.1

[a] q = quartet; t = triplet.

TABLE III. Characteristic Infrared Bands of $Cp_2(S_2CNR_2)Cl$ and $(MeCp)_2Zr(S_2CNR_2)Cl$ (R = Me, Et) Complexes.

S. No.	Peak Position (in cm^{-1})				Assignment
	Due to $Cp_2Zr(S_2CNMe_2)Cl$	Due to $Cp_2Zr(S_2CNEt_2)Cl$	Due to $(MeCp)_2Zr(S_2CNMe_2)Cl$	Due to $(MeCp)_2Zr(S_2CNEt_2)Cl$	
1	334 m	329 m	335 m, b	332 m, b[a]	ν(Zr–Cl)
2	358 m	353 m	355 m	332 m, b[a]	ν(Zr–S)
3	1525 s, b	1495 vs	1520 s, b	1498 s	ν(C$\cdots$N)
4	1000 sh	1010 s[b]	994 m	1008 m	ν(C$\cdots$S)
5 (i)[c]	3110 m	3110 m	3110 m	3105 m	ν(C–H)
(ii)	1440 m, b	1429 s	1450 m	1434 s	ν(C–C) (asymmetric ring breathing)
(iii)	1014 s	1010 s	1033 m	1032 m	ν(C–H) (in plane bending)
(iv)	805 vs	803 vs	811 vs	819 vs	ν(C–H) (bending out of plane deformation)
6	1147 m	1146 m	1142 m	1148 m	ν(C–N–C)
7	2920 m	2960 m	2935 m	2995 m, 2910 m	ν(C–H) aliphatic

[a] ν(Zr–Cl) and ν(Zr–S) overlap to give a single broad band. [b] Overlaps with ν(C–H) (in plane bending) band. [c] Infrared band characterising π-C_5H_5 and π-$CH_3C_5H_4$ rings.

bands due to the dithiocarbamate ligands are masked by cyclopentadienyl (and methylcyclopentadienyl) bands, but several assignments are possible. The 'thioureide' band (C$\cdots$N) near 1500 cm^{-1} is very characteristic of dithiocarbamates. The frequency of this band lies between that for C–N (1250–1350 cm^{-1}) and C=N (1640–1690 cm^{-1}) which suggests that this bond has some double bond character. Table III shows that both the complexes exhibit just one C–N band and one C–S band. It is assumed from this evidence that the C–S bonds are most likely equivalent. The spectra, therefore, indicate bidentate dithiocarbamate attachment. Fay *et al.* [5] have described the X-ray diffraction of $(\eta^5$-$C_5H_5)Zr[S_2CN(CH_3)_2]_3$ in which, because of the relatively small size of the cyclopentadienyl group, it is considered to occupy single axial coordination site in a pentagonal bipyramidal structure. On this analogy the cyclopentadienyl and methylcyclopentadienyl groups in the compounds included in this communication are assumed to occupy single coordination site.

On the whole then, the infrared data favour a five-coordinate structure for the above four compounds.

Nmr Spectra

Table II lists the positions of the resonance signals observed in the nmr spectra of the compounds. The observed nmr spectra favour a trigonal bipyramidal structure (with the two cyclopentadienyl and two methylcyclopentadienyl groups in *trans*-positions) for the above compounds.

The resonance signal due to the C_5H_4 portion of π-$CH_3C_5H_4$ is observed as a comparatively broad peak with some fine structure. This is probably due to the presence of the CH_3 group on the ring.

The intensities were determined by planimetric integration of these spectra. The integrated proton ratios correspond to the formula $Cp_2Zr(S_2CNR_2)Cl$

and $(MeCp)_2Zr(S_2CNR_2)Cl$ (R = Me, Et). Because of the symmetry involved in the above structure, it is not possible to discuss the stereochemical rigidity or non-rigidity in the dithiocarbamate portion of the complexes (because the same number of resonance signals for R groups will be observed whether $S_2C–N$ bond rotation is slow or fast).

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References

1 A. N. Bhat, R. C. Fay, D. F. Lewis, A. F. Lindmark and S. H. Strauss, *Inorg. Chem., 13,* 886 (1974).
2 D. F. Lewis and R. C. Fay, *J. Am. Chem. Soc., 96,* 3843 (1974).
3 J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White and E. N. Maslen, *J. Chem. Soc. Dalton,* 2082 (1973).
4 T. F. Brennan and I. Bernal, *Chem. Commun.,* 138 (1970); *Inorg. Chim. Acta, 7,* 283 (1973).
5 Alan Bruder, R. C. Fay, David F. Lewis and Alice Ann Sayler, *J. Am. Chem. Soc., 98,* 6932 (1976).
6 H. L. Klopping and G. J. M. Van der Kerk, *Recl. Trav. Chim. Pays-Bas, 70,* 917 (1951).
7 P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding and R. C. Srivastava, *J. Chem. Soc. A,* 2106 (1969).
8 E. Samuel, *Bull. Soc. Chim. Fr.,* 3548 (1966).
9 R. C. Fay and R. N. Lowry, *Inorg. Chem., 6,* 1512 (1967).
10 B. F. G. Johnson, K. H. Al obaidi and J. A. McCleverty, *J. Chem. Soc., A,* 1668 (1969).
11 A. Diomenicano, A. Vaciago, L. Zambonelli, P. L. Loader and L. M. Venanzi, *Chem. Commun.,* 476 (1966).
12 C. O'Connor, J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. A,* 84 (1969).
13 F. Bonati and R. Ugo, *J. Organometal. Chem., 10,* 257 (1967).
14 C. S. Harrel and E. O. Schlemper, *Acta Crystallogr., B 27,* 1964 (1971).
15 E. C. Alyea, B. S. Ramaswamy, A. N. Bhat and R. C. Fay, *Inorg. Nucl. Chem. Lett., 9,* 399 (1973).
16 M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse and I. F. Rendall, *Chem. Commun.,* 743 (1970); *J. Chem. Soc. Dalton,* 1052 (1972).
17 D. C. Bradley and M. H. Gitlitz, *Chem. Commun.,* 289 (1965); *J. Chem. Soc. A,* 1152 (1969).