Inorganica Chimica Acta, 53 (1981) L271–L273
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Sulphur Ligand Metal Complexes.
Part 13 [1]. Palladium(II) and Platinum(II) Complexes of Pentafluoroaryl Thioether Ligands

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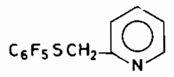
Received December 3, 1980

Introduction

Little is known about the effect electronegative fluoro substituents have on the donor properties of thioether ligands. Recently we examined the reactivity of the pentafluorophenyl substituted thioether ligands L^1–L^3 towards the group 6 metal carbonyls but only with L^2 could a stable complex be isolated [2]. The X-ray structure of the platinum complex *cis*-$PtCl_2(CF_3SCHMeCH_2SCF_3)$ showed the Pt–S distances to be only slightly shorter than the corresponding values in other thioether platinum complexes [3], and from studies on palladium(II) complexes of mixed sulphur–phosphorus donor ligands, it was concluded from electronic spectral results, that the ligand field characteristics of the fluorinated and unfluorinated analogues were similar [4]. In order to probe further the effect of fluoro substituents on the coordinating ability of thioether ligands we have investigated the reactivity of the ligands L^1–L^3 with the d^8 metals, Pd(II) and Pt(II). In this paper we report the synthesis and characterization of the following new complexes: *cis*-MCl_2L (M = Pd or Pt, L = L^1 or L^2) and *trans*-$PtCl_2L^3_2$. The ultraviolet photoelectron spectrum of L^1 is also reported and compared with other unfluorinated aryl sulphide ligands.

$L^1 = C_6F_5S(CH_2)_2SC_6F_5$ $\quad$ $L^3 = C_6F_5SEt$

$L^2 =$



Experimental

Physical measurements were made as previously described [2, 5]. The ligands were prepared following a general method for aryl sulphides [6] using pentafluorothiophenol (Aldrich Chemical Co.), sodium ethoxide and 1,2-dibromoethane (L^1), 2-picolychloride hydrochloride (L^2) or iodoethane (L^3). L^1 was obtained as a white solid, m.p. 127–30 °C, and the other ligands as viscous liquids. All ligands showed the expected parent molecular ions in their mass spectra.

The complexes were routinely dried *in vacuo.*

cis-$PdCl_2L^1$

To a methanol solution of Na_2PdCl_4 (0.294 g, 1 mmol) was added a suspension of the ligand L^1 (0.426 g, 1 mmol) in the same solvent and the mixture refluxed gently. The resulting orange precipitate was filtered and washed with methanol/water, methanol and diethylether. Yield 0.283 g (47%). *Anal.* Found: C, 27.8; H, 1.1, Cl, 11.6. Calcd. for $C_{14}H_4Cl_2F_{10}PdS_2$: C, 27.85; H, 0.7; Cl, 11.75%.

cis-$PtCl_2L^1$

To a toluene solution of L^1 (0.426 g, 1 mmol) was added $PtCl_2(PhCN)_2$ (0.472 g, 1 mmol) and the mixture refluxed for 20 min. The resulting yellow precipitate was recrystallized from acetone. Yield 0.455 g (64%). *Anal.* Found: C, 25.1; H, 1.2; Cl, 10.3. Calcd. for $C_{14}H_4Cl_2F_{10}PtS_2$: C, 24.3; H, 0.6; Cl, 10.2%.

cis-MCl_2L^2 *(M = Pd or Pt) and* trans-$PtCl_2L^3_2$

These were prepared from $MCl_2(PhCN)_2$ and the appropriate ligand following the above method. *cis*-$PdCl_2L^2$ was recrystallized from ethanol as an orange solid. M.p. 134–7 °C. *Anal.* Found: C, 32.8; H, 2.1; N, 2.7. Calcd. for $C_{12}H_6Cl_2F_5NPdS\cdot EtOH$: C, 32.7; H, 2.3; N, 2.7%. For *cis*-$PtCl_2L^2$ 24 hr refluxing was required to obtain the product as a yellow solid. *Anal.* Found: C, 25.25; H, 0.9; N, 2.2. Calcd. for $C_{12}H_6Cl_2F_5NPtS$: C, 25.9; H, 1.1; N, 2.5%. *trans*-$PtCl_2L^3_2$ was recrystallized as an orange solid from toluene. M.p. 135–40 °C. *Anal.* Found: C, 27.6; H, 1.9; Cl, 9.8. Calcd. for $C_{16}H_{10}Cl_2F_{10}PtS_2$: C, 26.6; H, 1.4; Cl, 9.8%.

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TABLE I. Vertical Ionization Potentials (eV) for Sulphide Ligands.[a]

Compound	IP_1	IP_2	IP_3	IP_4	IP_5
3,4-bis(methylthio)toluene	7.85	8.43	9.11	9.93	10.70
3,4-bis(ethylthio)toluene	7.78	8.28	9.01	9.79	10.45
1,3-bis(methylthio)benzene	8.09	8.34	9.66	10.23	10.99
L^1	9.07		9.70		11.65

[a] IP_2 and IP_5 are essentially lone pair orbitals localized on sulphur.

TABLE II. Electronic Spectral Data (340–700 nm) for the Complexes.

Complex	λ_{max}[a]	State
cis-$PdCl_2L^1$	422 (1077)	c
	417	d
cis-$PdCl_2(PhSCH_2CH_2SPh)$[b]	417 (2150)	e
	422	d
cis-$PdCl_2L^2$	407 (580)	e
	410	d
cis-$PtCl_2L^1$	397 (223)	c
	398	d
cis-$PtCl_2(PhSCH_2CH_2SPh)$[b]	370 (1550)	e
	390	d
cis-$PtCl_2L^2$	375sh (220)	e
	380sh	d
trans-$PtCl_2L^3_2$	410sh, 500sh	d
	405sh (170), 490sh (35)	c

[a] Absorption coefficients (l mol^{-1} cm^{-1}) are given in parenthesis. [b] From ref. 12. [c] Acetone. [d] Reflectance. [e] CH_2Cl_2.

Results and Discussion

Ultraviolet Photoelectron Spectra

Unfortunately the UV PES spectrum of L^3 could not be measured because of apparent damage to the detector. However the effect of the electronegative fluoro substituents on the ionization potentials of the sulphur lone pair electrons of L^1 is readily apparent (Table I). For R_2S (R = Me, Et *etc*) ligands the highest occupied molecular orbital, HOMO, is largely localized on the sulphur atom, but in a ligand such as L^1, the HOMOs on both sulphurs are coupled to form a symmetric (n_s) and an antisymmetric combination. In the spectrum of L^1, three bands were observed compared to the five bands observed for 3,4-bis(methylthio)toluene, 3,4-bis(ethylthio)toluene and 1,3-bis(methylthio)benzene. The peaks may be analysed following the work of Bock *et al.* [7] for 1,4-bis(methylthio)benzene. The first band at 9.07 eV probably arises from a (small) interaction of the antisymmetric combination of sulphur HOMOs with an aryl π orbital overlapping with the n_s combination. The second band (9.70 eV broad) is derived mainly from the aryl π orbital, while the third (11.65 eV) arises from the 'other' lone pair orbital (n_σ) on each sulphur. The fluoro electronegativity effect is most readily seen on comparison of this high ionization potential with the values (10.45–10.99 eV) found for the other aryl sulphides. Similar effects have been reported for $(CH_3)(CH_2Cl)S$ [5] and PF_3 [8].

The Complexes cis-*MCl_2L (M = Pd or Pt, L = L^1 or L^2) and* trans-*$PtCl_2L^3_2$*

The observation of a single strong band at 342 cm^{-1} assignable to a ν(Pt–Cl) absorption [9] and the similarity of the electronic spectrum (Table II) to spectra known *trans*-$PtCl_2L_2$ complexes [10] allows the formulation of the L^3 ligand complex as *trans*-$PtCl_2L^3_2$. For the L^1 and L^2 complexes the ν(M–Cl) bands cannot be identified with certainty from the expected [11, 12] ν(M–S) absorptions also occurring in the 300–350 cm^{-1} region. The electronic spectra of the complexes in the visible region are given in Table II and are characteristic of planar d^8 systems. While the assignment of the electronic spectral bands in this region remains under discussion it appears that they are essentially d–d in nature and give a reliable indication of the average ligand field exerted by the donor atoms [10, 12–14]. The band maxima of the *cis*-MCl_2L^1 (M = Pd or Pt) complexes fall in the range found for a wide range of unfluorinated thioether chelate complexes *cis*-MCl_2L, *viz.* for M = Pd λ_{max} = 385–430 nm, for M = Pt λ_{max} = 370–420 nm [12, 13], and if reflectance spectra are compared the λ_{max} positions are not markedly different from values found for *cis*-$MCl_2(PhSCH_2CH_2SPh)$ (M = Pd or Pt) [12]. However solvent effects do appear to be less important for the fluorinated thioether complexes, with reflectance and solution spectra being very similar. The spectral data for the complex, *trans*-$PtCl_2L^3_2$, is also similar to that observed for other *trans* thioether Pt complexes [10]. It therefore appears that similar ligand fields are exhibited by thioethers and their fluorinated analogues. The observations of the high ionization potentials observed for L^1 as well as the low pK_a of pentafluorothiophenol (2.68) as compared to thiophenol (6.43) [15] would imply that the S → M σ donor interactions must be significantly weakened as a result of the pentafluoroaryl substituents. Hence the M → S π back bonding must increase, but only sufficiently to compensate for the loss in σ bonding. Support for this conclusion comes from the single crystal structure of the fluorinated thioether complex *cis*-$PtCl_2(CF_3SCHMeCH_2SCF_3)$ where the Pt–S bond is not significantly different from the Pt–S distances found in other platinum complexes [3].

In conclusion then, the present study reinforces our earlier findings [16] that the metal–thioether linkage is particularly flexible, making it a suitable ligand for metals in proteins. When thioethers are bound to zero valent metals, *e.g.* Cr(0), S → M π bonding is important [17] but in monovalent Cu(I) complexes there is a considerable variation in Cu–S π bonding [16]. In the divalent Cu(II) complex, $[Cu(MeSCH_2CH_2SMe)_2](BF_4)_2$, the Cu–S bond can be regarded as essentially single [18]. The extent of the M → S π component is sensitive to the nature of: (a) the metal, (b) the ancillary ligands, and (c) the substituents on the thioether sulphur.

Acknowledgements

We thank the New Zealand University Grants Committee for financial support, Messrs W. J. Kermode and A. A. Trow for experimental assistance and Dr. E. N. Baker for useful discussions.

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