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The X-ray crystal structure of di-η^5-cyclopentadienylthiophenolatoamminemolybdenum(IV) hexafluorophosphate solvate, $[Mo(\eta^5\text{-}C_5H_5)_2(NH_3)(SC_6H_5)][PF_6] \cdot (CH_3)_2CO$

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Abstract

Crystals of $[Mo(\eta^5\text{-}C_5H_5)_2(NH_3)(SC_6H_5)][PF_6] \cdot (CH_3)_2CO$ solvate are monoclinic, space group $P2_1/n$, a 9.777(1), b 11.6343(2), c 19.656(4) Å, β 93.60(1)°, V 2231.46 Å^3, $Z = 4$, D_c 1.617 g cm^{-3}, μ(Mo-K_α) 7.21 cm^{-1}. The structure was solved by Patterson and difference Fourier electron density synthesis and refined to $R(F) = 0.047$ and $R_w(F) = 0.057$ for 3293 observed reflections. The molybdenum atom has the usual distorted tetrahedral geometry comprising the two Mo–Cp ($Cp = \eta^5\text{-}C_5H_5$) ring normals (Mo–Cp 1.988(13), 1.989(15) Å), one Mo–NH_3 (Mo–N 2.226(12) Å), and one Mo–SC_6H_5 (Mo–S 2.465(5) Å). Extended HMO and steric energy calculations were made in order to account for the geometry adopted by the thiolato ligand in this complex.

Introduction

We recently described the structures of a number of dicyclopentadienylmetal dithiolato complexes [1] and also the results of complementary thermochemical studies [2]. Our objective in this work is to obtain a detailed understanding of the factors, particularly electronic and steric effects, that determine the precise structures adopted by these complexes. In our previous work, we have found that the relative orientations of the SR ligands can be quite different, and seem to depend essentially on steric effects [2c]. In order to extend our knowledge of these systems, we have determined the structure of a monothiolato dicyclopentadienylmetal derivative in which the fourth site is occupied by a small neutral ligand, giving a singly

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charged cationic complex, viz. $[Mo(Cp)_2(SPh)(NH_3)]^+$, which was crystallized as the PF_6^- salt, solvated with one acetone molecule.

Experimental

Crystal data

$[C_{16}H_{18}NSMo]^+[PF_6]^- \cdot C_3H_6O$, $M_r = 543.37$, monoclinic, space group $P2_1/n$, a 9.777(1), b 11.6343(2), c 19.656(4) Å, β 93.60(1)°, V 2231.46 Å^3, $Z = 4$, D_c 1.617 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ 7.21 cm^{-1}.

Data collection

Crystals were grown at room temperature during one week by slow diffusion of ether into a (previously filtered) saturated solution of $[Mo(Cp)_2(NH_3)(SC_6H_5)[PF_6]$ in acetone. All the manipulations were carried out under N_2 by Schlenk techniques and the solvents were dried by conventional methods [3]. X-ray measurements were made with an Enraf–Nonius CAD-4 diffractometer and graphite monochromatized Mo-K_α radiation (λ 0.71069 Å). Cell dimensions and the orientation matrix were obtained by least-squares refinement of setting angles for 25 automatically centered reflections with $11.5° \leqslant \theta \leqslant 15.0°$. The intensities of 3293 independent reflections in the range $1.5° \leqslant \theta \leqslant 25.0°$ were measured by the ω–2θ scan mode with ω scan widths of $0.80 + 0.35\tan\theta°$ and scan speeds of 1.28–6.80 degree min^{-1}. The data were corrected for Lorentz and polarization effects.

Structure determination

The 3082 reflections that satisfied the criterion $F > 3.5\sigma(F)$ were used for the structure solution and refinement. The Mo position was located from a Patterson map and the O, N, S, P, and F positions from subsequent difference Fourier syntheses. Least-squares refinements with isotropic temperature factors for all the non hydrogen atoms gave $R = 0.10$. Data were then corrected for absorption using DIFABS [4] (minimum and maximum absorption correction 0.881 and 1.124, respectively). Refinement was continued with anisotropic thermal parameters to $R = 0.059$. The hydrogen atoms of the cyclopentadienyl rings were placed in calculated positions, while those of the NH_3 group were located from the ΔF map and included in the refinement with individual isotropic thermal parameters. The weighting scheme $w = 3.428/[\sigma^2|F| + 0.00013F^2]$ gave acceptable agreement analyses. Final refinement gave $R = 0.047$ and $R_w = 0.057$.

Final atomic positional parameters for the refined atoms are given in Table 1. Tables of anisotropic displacement factor coefficients and positional parameters for idealised hydrogen atoms and lists of observed and calculated structure factors are available from the authors. All computations required to solve and refine the structure were made by use of SHELX76 [5]; drawings were made by use of ORTEP [6]. Atomic scattering values were taken from International Tables [7].

EHMO and steric energy calculations

EHMO calculations were performed with the ICON8 program [8] with modified H_{ij}'s [9] and the starting geometry found in the crystal structure. The basis set for the molybdenum atom consisted of $4d$, $5s$, and $5p$ orbitals; only $3s$ and $3p$ orbitals were considered for the sulphur atom. The s and p orbitals were described by single Slater type wavefunctions, and the d orbitals as contracted linear combinations of

Table 1

Fractional atomic coordinates ($\times 10^4$) for $[MoCp_2(NH_3)(SC_6H_5)][PF_6]\cdot(CH_3)_2CO$

	x	y	z	U_{eq} or U_{iso}
Mo	6311(1)	3851	8677	34(.3)
S	4736(2)	3363(1)	9566(1)	41(.3)
N	7229(6)	4747(5)	9597(3)	47(2)
C(11)	3351(6)	2451(5)	9302(3)	41(2)
C(12)	2521(7)	2063(6)	9801(4)	56(2)
C(13)	1401(7)	1361(7)	9642(5)	70(3)
C(14)	1104(7)	1028(7)	8984(15)	69(3)
C(15)	1912(7)	1393(6)	8474(4)	62(3)
C(16)	3024(7)	2101(5)	8635(3)	51(2)
C(21)	4323(6)	4726(6)	8199(3)	54(2)
C(22)	5046(8)	4339(7)	7666(3)	66(3)
C(23)	6310(8)	4957(8)	7691(4)	74(3)
C(24)	6343(7)	5690(6)	8255(4)	59(2)
C(25)	5121(7)	5534(5)	8570(3)	50(2)
C(31)	6748(10)	1865(7)	8841(5)	80(3)
C(32)	6599(9)	2066(7)	8190(5)	77(3)
C(33)	7616(12)	2795(8)	7991(5)	86(3)
C(34)	8436(8)	3078(7)	8603(7)	95(4)
C(35)	7813(10)	2459(8)	9114(4)	79(3)
C(50)	28(8)	3933(6)	6519(4)	59(2)
O(51)	−1159(6)	3974(7)	6607(3)	109(3)
C(51)	529(10)	4129(8)	5814(4)	146(4)
C(52)	1095(10)	3709(10)	7090(5)	172(4)
P	4327(2)	1492(2)	6233(1)	60(.3)
F(1)	4969(6)	1213(6)	5545(3)	128(3)
F(2)	5495(9)	915(11)	6647(5)	224(5)
F(3)	3697(11)	264(8)	6192(4)	192(5)
F(4)	3676(6)	1746(7)	6923(3)	125(3)
F(5)	4996(16)	2600(8)	6285(5)	287(7)
F(6)	3054(9)	1843(10)	5848(4)	221(4)
H(1N)	6798(81)	5204(74)	9833(40)	81(15)
H(2N)	7900(82)	5108(73)	9528(39)	81(15)
H(3N)	7466(80)	4221(77)	9968(41)	81(15)

two Slater type wave functions. The orbitals, exponents and parameters for molybdenum are listed in Table 2 and those for other atoms were as given previously [8]. Steric energy calculations were made with the program EENY2 [10].

Table 2

Orbital exponents and parameters used in the EHMO calculations

Orbital	$-H_{ii}$ (eV) [a]	Slater exponents		Coefficients		Ref.
		1	2	C_1	C_2	
$5s$	8.77	1.96				b
$5p$	5.60	1.90				b
$4d$	11.60	4.54	1.90	0.5899	0.5899	b,c

[a] 1 eV = 96.4845 kJ mol^{-1}. [b] M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, T. Yoshida, and S. Otsuka, J. Am. Chem. Soc., 103 (1981) 5772. [c] J.W. Richardson, W.C. Nieuwpoort, R.R. Powell, and W.E. Edgell, J. Chem. Phys., 36 (1962) 1057.

Results and discussion

The structure of the molecule is shown in Fig. 1, along with the atom numbering system. Bond lengths and angles are given in Table 3.

The crystal structure consists of discrete $[Mo(Cp)_2(NH_3)(SC_6H_5)]^+$ cations, $[PF_6]^-$ anions, and $(CH_3)_2CO$ solvent molecules. The metal is coordinated to two η^5-cyclopentadienyl rings, the nitrogen atom of the ammine ligand, and the sulphur atom of the thiophenolate ligand, in a distorted tetrahedral environment, with an angle between the ring normals of 134.9(7)°. The Mo–S bond length is similar to those observed in other $Mo(Cp)_2$ derivatives containing S-bonded ligands [2b], and the Mo–N bond length lies in the normal range of Mo–N distances for $[Mo(Cp)_2LL']$ complexes [11]. The N–Mo–S angle is a few degrees smaller than is usual for $Mo(Cp)_2$ species coordinated to two monodentate ligands [2b,11], an exception being $[Mo(Cp)_2(S\text{-}^tBu)_2]$ where the S–Mo–S angle is 71.1° [2c].

A striking feature of the structure is the position adopted by the phenyl ring, which lies almost in the plane containing Mo, N, and S atoms, as seen clearly in Fig. 2. This contrasts sharply with the geometry observed in the $[Ti(Cp)_2(SPh)_2]$ complex [2a], where one of the phenyl rings is above and the other below the corresponding plane (here defined by S, Ti, and S), pointing almost in opposite directions.

In an attempt to define the reasons for the geometry adopted by the thiolato ligand in this complex, we have examined the steric and electronic energy surfaces for the two torsion angles α, N–Mo–S–C(11) and β, Mo–S–C(11)–C(16). The NH_3 ligand was kept fixed.

A steric energy map of the α,β surface, calculated using EENY2, showed that within an energy barrier limit of 100 kJ mol^{-1} there is a continuous valley that connects three shallow minima. The global minimum (α 157°, β 234°) had an energy (20 kJ mol^{-1}) slightly lower than the other two (α 171°, β 171°, U 30 kJ mol^{-1} (= structure found) and α 0°, β 270°, U 28 kJ mol^{-1}). EHMO calculations, however, showed the experimental structure to be preferred by ~ 12 kJ mol^{-1}.

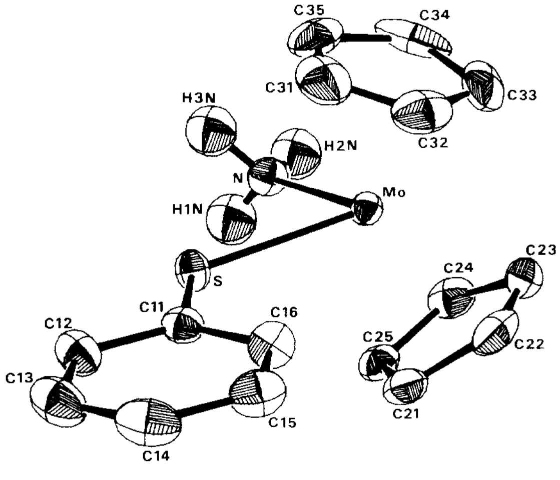

Fig. 1. Molecular structure of $[Mo(Cp_2)(NH_3)(SC_6H_5)]^+$ with 30% thermal ellipsoids.

Table 3

Bond lengths (Å) and angles (deg) for $[Mo(Cp)_2(NH_3)(SC_6H_5)][PF_6]\cdot(CH_3)_2CO$

Bond lengths			
S–Mo	2.465(5)	N–Mo	2.226(12)
C(21)–Mo	2.339(13)	C(31)–Mo	2.368(17)
C(22)–Mo	2.345(13)	C(32)–Mo	2.312(16)
C(23)–Mo	2.327(14)	C(33)–Mo	2.275(15)
C(24)–Mo	2.295(14)	C(34)–Mo	2.277(15)
C(25)–Mo	2.280(13)	C(35)–Mo	2.315(15)
C(11)–S	1.773(13)	H(1N)–N	0.84(17)
C(11)–C(12)	1.386(18)	H(2N)–N	0.80(17)
C(12)–C(13)	1.386(20)	H(3N)–N	0.97(18)
C(13)–C(14)	1.364(23)		
C(14)–C(15)	1.381(22)		
C(15)–C(16)	1.384(19)	Mo–Cp(21–25) [a]	1.988(13)
C(16)–C(11)	1.392(17)	Mo–Cp(31–35) [b]	1.989(15)
Bond angles			
S–Mo–N	76.4(4)	Cp(21–25)–Mo–Cp(31–35)	134.9(7)
Mo–N–H(1N)	124(11)	H(1N)–N–H(2N)	102(15)
Mo–N–H(2N)	114(12)	H(2N)–N–H(3N)	107(14)
Mo–N–H(3N)	112(10)	H(1N)–N–H(3N)	95(13)
Mo–S–C(11)	115.5(5)	C(21)–C(22)–C(23)	107.1(13)
S–C(11)–C(12)	117.3(10)	C(22)–C(23)–C(24)	108.1(12)
S–C(11)–C(16)	125.2(10)	C(23)–C(24)–C(25)	107.2(13)
C(11)–C(12)–C(13)	121.4(14)	C(24)–C(25)–C(21)	108.8(12)
C(12)–C(13)–C(14)	120.0(14)	C(25)–C(21)–C(22)	108.7(13)
C(13)–C(14)–C(15)	120.2(13)	C(31)–C(32)–C(33)	110.5(17)
C(14)–C(15)–C(16)	119.6(14)	C(32)–C(33)–C(34)	106.0(15)
C(15)–C(16)–C(11)	121.3(13)	C(33)–C(34)–C(35)	103.7(15)
C(16)–C(11)–C(12)	117.5(12)	C(34)–C(35)–C(31)	109.8(16)
		C(35)–C(31)–C(32)	109.9(18)

[a] Denotes ring normal to C(21)–C(25). [b] Denotes ring normal to C(31)–C(35).

Although exact correlation between the energies produced by the two types of calculations is not possible, our results to indicate that there is a very broad conformational energy surface for this molecular structure, which therefore must

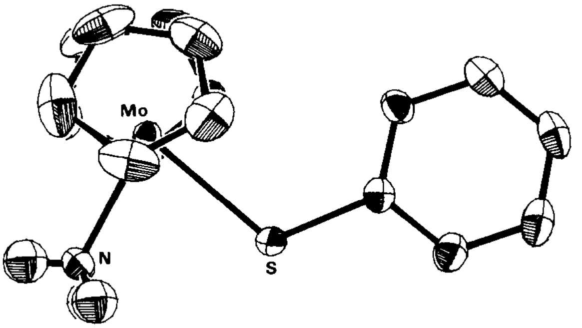

Fig. 2. Projection of the cation $[Mo(Cp_2)(NH_3)(SC_6H_5)]^+$ onto the Mo,N,S plane.

arise from a delicate balance between electronic and steric factors. With such an extensive surface, it is also possible that solid state packing effects may be important.

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