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STEREOCHEMISTRY OF TWO DICYCLOPENTADIENYLMOLYBDENUM COMPLEXES. MOLECULAR STRUCTURE OF DI-η^5-CYCLOPENTADIENYL-*N*-(α,α'-DIMETHYLMETHOXY)PYRAZOLATOMOLYBDENUM(IV) HEXAFLUOROPHOSPHATE AND DI-η^5-CYCLOPENTADIENYLBISPYRAZOLATOMOLYBDENUM(IV)

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Summary

Crystals of di-η^5-cyclopentadienyl-*N*-(α,α'-dimethylmethoxy)pyrazolatomolybdenum(IV) hexafluorophosphate, $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3C(CH_3)_2O)](PF_6)$, **1**, are monoclinic space group $P2_1/n$ with a 12.943(2) Å, b 10.895(2) Å, c 13.623(2) Å, β 105.22(1)° and $Z = 4$. Crystals of di-η^5-cyclopentadienylbispyrazolatomolybdenum(IV), $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3)_2]$, **2**, are monoclinic space group $P2_1/n$ with a 8.510(1) Å, b 9.631(1) Å, c 18.264(3) Å, β 102.73(1)° and $Z = 4$. The structures were solved by Patterson and difference electron density syntheses and refined by least-squares to R_1 of 0.046 for 3791 reflexions for **1** and R_1 of 0.029 for 2109 reflexions for **2**.

The structure of compound **1** consists of discrete cations with an approximate C_{2v} symmetry at the molybdenum atom and PF_6^- anions. The molybdenum atom is at an average distance of 1.995 Å from the cyclopentadienyl rings, and the angle between these normals is 128.8°. The Mo–O and Mo–N bond lengths are 2.026(2) and 2.123(3) Å, and the O–Mo–N bond angle is 75.4(1)°.

The structure of compound **2** consists of discrete molecules with an approximate C_s symmetry at the molybdenum. The molybdenum atom lies at an average distance of 1.982 Å from the cyclopentadienyl rings and the angle between the ring normals is 133.2°. The Mo–N bond lengths are 2.166(3) and 2.157(3) Å and the N–Mo–N bond angle is 83.3(1)°.

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Introduction

Reactions of some metallocene derivatives with pyrazole and related ligands to give a wide range of mono- and bi-nuclear complexes were recently reported [1]. In one of those reactions an unexpected mono-nuclear complex was obtained and coordination of the solvent, acetone, was assumed in its characterisation. The X-ray structural characterisation of this compound is described here, and confirms the postulated molecular structure for $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3C(CH_3)_2O)](PF_6)$, **1**.

The molecular structure of the neutral bispyrazolate derivative $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3)_2]$, **2**, used as a ligand in an unsuccessful attempt to prepare binuclear complexes, is also reported. This shows the geometry of the molecule in the crystal to be unfavourable for the coordination with another metal to produce a binuclear complex.

TABLE 1

CRYSTALLOGRAPHIC DATA AND ENRAF-NONIUS CAD-4 DATA COLLECTION PARAMETERS

	1	**2**
formula	$[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3C(CH_3)_2O)](PF_6)$	$[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3)_2]$
space group	$P2_1/n$	$P2_1/n$
M_r	493.2	360.3
a, A°	12.943(2)	8.510(1)
b, A°	10.895(2)	9.631(1)
c, A°	13.623(2)	18.264(3)
β, deg	105.22(1)	102.73(1)
V	1853.7	1460.1
Z	4	4
d_{calcd}, g/cm^3	1.77	1.62
crystal size, mm	irregular	irregular
radiation	Mo-$K_{\bar{\alpha}}$ (λ 0.71073 Å)	Mo-$K_{\bar{\alpha}}$ (λ 0.71073 Å)
μ(Mo-K_α), cm^{-1}	7.32	7.97
scan type	$\omega - 2\theta$	$\omega - 2\theta$
scan width ($\Delta\omega$),deg	$0.85 + 0.35 \tan\theta$	$0.85 + 0.35 \tan\theta$
maximum counting time, s	60	60
collection range	$\pm h, +k, +l$ $3.0 < 2\theta < 50.0$	$\pm h, +k, +l$ $3.0 < 2\theta < 50.0$
no. of unique data	4460	2564
no. of data $F < 3\sigma(F)$	669	455
decay during collection	none	5%, linear
R_{int}	0.0058	0.0057
no. of variables	247	206
R_1 [a]	0.046	0.029
R_2 [a]	0.070	0.031
largest shift/error value on final cycle	0.12	0.49
largest peak in final difference Fourier, e/A°^{3}	0.45	1.12

[a] $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$, $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.

Experimental

Crystals of **1** and **2** suitable for diffraction measurements were kindly supplied by Dr. M.J. Calhorda of this Institute [1]. Preliminary cell dimensions and space group were determined from Weissenberg and precession photographs. Diffraction measurements were made on a Enraf–Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo-$K_{\bar{\alpha}}$ radiation. Unit cells and orientation matrix were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index and least-squares routines. The intensity data were collected at room temperature using the ω–2θ technique and a scan range determined by $\Delta\omega = (0.85 + 0.35 \text{ tang } \theta)^\circ$ with a total of 96 steps per scan, 16 steps for the background on each side of the peak and 64 steps for the scan through the peak. Standard data-collection procedures were previously summarized [2] and the pertinent crystallographic parameters for both crystals are listed on Table 1. Data were corrected for Lorentz and polarization effects and merged to a unique set of reflections. All calculations required to solve and refine the structures were done using the system of programs SHELX [3] and were carried out at an IBM-360 computer at Instituto Superior Tècnico. Atomic scattering factors were taken from ref. 4.

Structure analyses and refinement

Both structures were solved by a combination of Patterson and difference Fourier methods and refined by least-squares.

In the case of compound **2**, the assignment of the N and C atoms of the pyrazolate ligands adjacent to the N atom which is coordinated to the Mo atom, was initially made by considering the height of the peaks in the ΔF map. However, all the other possible combinations were tried and refined isotropically, but abnormal thermal parameters resulted for these atoms compared with those obtained in the initial assignement. Thus this was considered to be the correct one, and was subsequently used in all the refinements.

Some cycles of refinement with isotropic temperature factors for all the nonhydrogen atoms gave $R_1 = 0.11$ for **1** and $R_1 = 0.074$ for **2**. Refinement was then continued with anisotropic thermal parameters. The hydrogen atoms were introduced at their calculated positions with a fixed C–H distance of 1.08 Å and refining each hydrogen isotropically in **2** and in three different groups with the same U_{iso} in **1**. The weighting scheme $w = K/(\sigma^2(F_0) + |g|F_0^2)$ was applied with the refined values of $K = 3.212$ and $g = 0.00054$ for **1** and $K = 2.399$ and $g = 0.00013$ for **2**. No absorption correction was applied, the linear absorption coefficients being 7.32 cm^{-1} for **1** and 7.97 cm^{-1} for **2**. Six low angle and strong reflections thought to be affected by extinction were removed from the data in **1**. The final refinements converged at $R_1 = 0.046$ and $R_2 = 0.070$ for **1** and $R_1 = 0.029$ and $R_2 = 0.031$ for **2**.

Final atomic positional parameters and anisotropic thermal parameters for the nonhydrogen atoms are listed in Table 2 for **1** and in Table 3 for **2**. Selected interatomic distances and angles are listed in Table 4 for **1** and in Table 5 for **2**.

The calculated positional parameters and the refined thermal parameters for the hydrogen atoms, tables of some least-squares, and lists of observed and calculated structure factors are available from the authors.

(Continued on p. 58)

TABLE 2

POSITIONAL AND THERMAL PARAMETERS[a] $(\times 10)^4$ FOR $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3C(CH_3)_2O)][PF_6]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	556.8(2)	1734.2(2)	2765.7(2)	366(2)	359(2)	470(2)	47(1)	129(1)	21(1)
O	380(2)	1123(2)	4117(2)	478(12)	340(11)	433(11)	22(9)	118(9)	−29(9)
N(1)	1033(3)	3238(2)	3774(3)	515(18)	346(15)	740(21)	22(13)	163(16)	−64(11)
N(2)	1000(3)	3042(3)	4750(3)	509(17)	408(15)	622(18)	−64(13)	100(14)	−55(12)
C(1)	1393(3)	4381(4)	3724(4)	601(24)	381(19)	1239(40)	98(23)	312(25)	−25(17)
C(2)	1620(4)	4907(4)	4697(4)	658(26)	387(20)	1226(40)	−165(24)	242(26)	−108(18)
C(3)	1339(4)	4030(4)	5334(4)	687(26)	470(21)	900(30)	−202(21)	99(23)	−34(19)
C(10)	615(3)	1824(3)	5003(3)	510(19)	397(17)	474(18)	−15(13)	96(15)	−42(13)
C(11)	−382(4)	2011(4)	5376(4)	731(27)	618(24)	791(28)	−171(21)	387(23)	−76(21)
C(12)	1506(4)	1220(4)	5821(3)	766(28)	612(24)	505(20)	41(18)	−113(19)	−13(21)
C(21)	2430(4)	1583(5)	3164(5)	397(21)	762(32)	1046(40)	−171(27)	127(23)	50(19)
C(22)	2062(3)	393(4)	3339(4)	522(22)	778(30)	841(29)	140(23)	239(21)	292(21)
C(23)	1414(3)	−14(4)	2450(4)	521(22)	516(22)	1078(35)	−74(22)	265(23)	81(17)
C(24)	1417(4)	869(5)	1678(3)	690(27)	946(35)	682(26)	−82(25)	299(22)	258(26)
C(25)	2062(4)	1878(5)	2181(5)	575(26)	769(32)	1278(48)	257(30)	543(31)	68(22)
C(31)	−628(4)	1744(7)	1217(4)	663(32)	1649(75)	556(26)	−36(31)	78(23)	363(36)
C(32)	−1080(4)	1023(5)	1815(5)	500(23)	677(29)	1067(39)	−73(28)	−84(25)	−1(21)
C(33)	−1327(3)	1797(5)	2492(4)	381(20)	1119(47)	740(30)	286(28)	103(20)	131(22)
C(34)	−999(4)	2920(6)	2352(5)	567(28)	892(36)	1089(43)	−182(34)	−69(28)	349(28)
C(35)	−522(4)	2937(6)	1549(5)	631(29)	1022(40)	1015(41)	640(36)	32(28)	101(28)
P	5942(1)	1983(1)	3808(1)	618(6)	554(5)	608(6)	46(4)	219(5)	68(5)
F(1)	6468(4)	955(4)	3336(5)	1923(51)	828(27)	3372(76)	−492(37)	1670(55)	71(29)
F(2)	6658(5)	2917(5)	3429(5)	2525(69)	1126(32)	2543(70)	−228(38)	1851(62)	−490(38)
F(3)	5411(5)	3108(4)	4229(4)	2033(53)	1500(44)	1440(40)	−123(28)	964(39)	640(34)
F(4)	5227(5)	1067(6)	4138(6)	2248(61)	1502(51)	3607(94)	660(54)	2010(70)	−92(45)
F(5)	5149(7)	2216(10)	2800(3)	2379(76)	3244(99)	859(32)	−52(41)	−36(37)	461(74)
F(6)	6767(6)	1998(7)	4871(5)	2061(69)	2600(80)	1522(51)	135(42)	−737(49)	570(50)

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[a] Numbers in parentheses in this and subsequent tables are the standard deviations from the least squares refinement.

TABLE 3

POSITIONAL AND THERMAL PARAMETERS ($\times 10^4$) FOR $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3)_2]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	6113.3(3)	5214.2(3)	3503.1(1)	341(2)	345(2)	323(2)	9(1)	69(1)	−17(1)
N(1)	5794(3)	4566(3)	2349(1)	466(15)	429(16)	367(15)	−10(12)	122(12)	26(12)
N(2)	6681(4)	5213(3)	1908(2)	614(19)	507(17)	440(17)	33(13)	226(14)	−16(14)
N(3)	4728(3)	3361(3)	3596(2)	384(15)	384(16)	430(16)	−6(12)	118(12)	−31(11)
N(4)	3584(3)	3333(3)	4017(2)	537(18)	557(19)	417(17)	−90(13)	179(14)	−165(14)
C(1)	5949(5)	4911(4)	1204(2)	861(30)	547(24)	396(20)	54(17)	220(20)	169(20)
C(2)	4583(5)	4108(4)	1171(2)	750(26)	500(22)	406(21)	−76(17)	−10(18)	140(20)
C(3)	4531(4)	3910(3)	1907(2)	483(20)	427(20)	503(22)	−123(16)	22(17)	20(15)
C(4)	3196(5)	2006(4)	4063(2)	671(25)	623(25)	425(21)	−31(18)	108(19)	−27(20)
C(5)	4077(5)	1143(4)	3700(2)	633(24)	420(21)	550(23)	8(17)	−5(19)	−133(17)
C(6)	5024(6)	2051(4)	3409(2)	505(21)	406(20)	591(23)	−41(17)	110(18)	34(15)
C(11)	4350(4)	6411(4)	4019(2)	658(25)	485(22)	567(24)	3(17)	284(21)	121(18)
C(12)	5612(5)	7317(3)	3969(2)	749(26)	370(19)	462(21)	−44(15)	96(19)	34(17)
C(13)	5583(5)	7562(4)	3199(2)	624(24)	422(20)	480(21)	67(16)	123(18)	33(17)
C(14)	4280(4)	6842(4)	2785(2)	587(23)	421(20)	498(22)	9(16)	−15(18)	147(16)
C(15)	3528(4)	6107(4)	3272(2)	434(20)	429(21)	803(28)	11(19)	87(19)	112(15)
C(21)	8327(4)	3807(4)	3648(2)	372(19)	662(25)	546(23)	−6(18)	78(17)	143(16)
C(22)	8790(4)	5186(4)	3513(2)	336(17)	887(30)	518(22)	179(21)	96(16)	−24(18)
C(23)	8604(4)	5992(4)	4132(2)	413(19)	556(24)	616(25)	97(19)	−76(18)	−141(16)
C(24)	8050(4)	5119(4)	4653(2)	429(19)	580(23)	401(18)	9(16)	−37(15)	−5(15)
C(25)	7914(4)	3788(4)	4356(2)	406(18)	496(21)	436(20)	95(16)	−15(15)	28(14)

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $[Mo(\eta^5\text{-}C_5H_5)_2\text{-}(N_2C_3H_3\text{-}C(CH_3)_2O)][PF_6]$

Bond distances			
Mo–N(1)	2.123(3)	Mo–O	2.026(2)
Mo–C(21)	2.347(5)	Mo–C(31)	2.259(5)
Mo–C(22)	2.396(4)	Mo–C(32)	2.307(5)
Mo–C(23)	2.301(5)	Mo–C(33)	2.368(5)
Mo–C(24)	2.278(5)	Mo–C(34)	2.333(6)
Mo–C(25)	2.295(6)	Mo–C(35)	2.280(6)
av. Mo–C	2.316(16)		
C(21)–C(22)	1.423(7)	C(31)–C(32)	1.369(9)
C(22)–C(23)	1.354(6)	C(32)–C(33)	1.348(8)
C(23)–C(24)	1.425(7)	C(33)–C(34)	1.325(9)
C(24)–C(25)	1.440(7)	C(34)–C(35)	1.390(10)
C(25)–C(21)	1.337(9)	C(35)–C(31)	1.372(10)
av. C–C	1.378(26)		
N(1)–N(2)	1.359(5)	O–C(10)	1.392(4)
N(1)–C(1)	1.338(5)	N(2)–C(10)	1.489(5)
N(2)–C(3)	1.342(5)	C(10)–C(11)	1.519(7)
C(1)–C(2)	1.403(8)	C(10)–C(12)	1.527(5)
C(2)–C(3)	1.401(7)		
P–F(1)	1.537(6)	P–F(4)	1.507(7)
P–F(2)	1.553(7)	P–F(5)	1.504(6)
P–F(3)	1.585(6)	P–F(6)	1.558(6)
Bond angles			
N(1)–Mo–O	75.4(1)		
N(2)–N(1)–Mo	115.7(2)		
C(10)–O–Mo	123.8(2)		
C(25)–C(21)–C(22)	109.9(4)	C(35)–C(31)–C(32)	111.6(6)
C(21)–C(22)–C(23)	107.7(4)	C(31)–C(32)–C(33)	105.3(5)
C(22)–C(23)–C(24)	108.6(4)	C(32)–C(33)–C(34)	109.7(6)
C(23)–C(24)–C(25)	106.1(4)	C(33)–C(34)–C(35)	110.5(6)
C(24)–C(25)–C(21)	107.6(5)	C(34)–C(35)–C(31)	102.7(6)
av. C–C–C	108.0(16)		
C(3)–N(2)–N(1)	111.4(3)	O–C(10)–C(11)	110.6(3)
C(1)–N(1)–N(2)	107.3(4)	N(2)–C(10)–C(12)	108.5(3)
N(1)–C(1)–C(2)	108.7(5)	O–C(10)–N(2)	107.4(3)
C(1)–C(2)–C(3)	106.4(4)	C(12)–C(10)–C(11)	111.0(3)
C(2)–C(3)–N(2)	106.2(4)	O–C(10)–C(12)	110.3(3)
		N(2)–C(10)–C(11)	108.9(3)

Description of the crystal structures and discussion

Di-η^5-cyclopentadienyl-N-(α,α'-dimethylmethoxy)pyrazolatomolybdenum(IV) hexafluorophosphate, 1

The crystal structure of **1** is composed of discrete $[Mo(\eta^5\text{-}C_5H_5)_2\text{-}(N_2C_3H_3C(CH_3)_2O)]^+$ cations (Fig. 1) and PF_6^- anions at general positions in the unit cell. To a good approximation the cation has a C_{2v} point symmetry at the metal atom and the anion has an approximate O_h symmetry. The metal atom is coordinated to two η^5-cyclopentadienyl rings and to a bidentate ligand from the reaction

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3)_2]$

Bond distances			
Mo–N(1)	2.157(3)	Mo–N(3)	2.166(3)
Mo–C(11)	2.256(4)	Mo–C(21)	2.288(4)
Mo–C(12)	2.274(4)	Mo–C(22)	2.274(4)
Mo–C(13)	2.349(3)	Mo–C(23)	2.302(3)
Mo–C(14)	2.390(3)	Mo–C(24)	2.368(3)
Mo–C(15)	2.313(4)	Mo–C(25)	2.368(3)
av. Mo–C	2.318(6)		
C(11)–C(12)	1.402(6)	C(21)–C(22)	1.422(6)
C(12)–C(13)	1.421(5)	C(22)–C(23)	1.408(6)
C(13)–C(14)	1.384(5)	C(23)–C(24)	1.425(6)
C(14)–C(15)	1.397(6)	C(24)–C(25)	1.387(5)
C(15)–C(11)	1.419(5)	C(25)–C(21)	1.413(5)
av. C–C	1.408(7)		
N(1)–N(2)	1.370(4)	N(3)–N(4)	1.368(4)
N(1)–C(3)	1.351(4)	N(3)–C(6)	1.344(4)
N(2)–C(1)	1.331(5)	N(4)–C(4)	1.327(5)
C(1)–C(2)	1.387(6)	C(4)–C(5)	1.383(6)
C(2)–C(3)	1.369(5)	C(5)–C(6)	1.373(6)
Bond angles			
N(1)–Mo–N(3)	83.3(1)	N(2)–N(1)–Mo	118.5(2)
C(3)–N(1)–Mo	129.2(2)	N(4)–N(3)–Mo	121.8(2)
C(6)–N(3)–Mo	128.2(2)	C(25)–C(21)–C(22)	107.7(3)
C(15)–C(11)–C(12)	106.8(3)	C(21)–C(22)–C(23)	107.0(4)
C(11)–C(12)–C(13)	108.7(3)	C(22)–C(23)–C(24)	108.8(3)
C(12)–C(13)–C(14)	107.2(3)	C(23)–C(24)–C(25)	107.2(3)
C(13)–C(14)–C(15)	109.3(3)	C(24)–C(25)–C(21)	109.3(3)
C(14)–C(15)–C(11)	108.0(3)		
av. C–C–C	108.0(6)		
C(3)–N(1)–N(2)	109.3(3)	C(6)–N(3)–N(4)	108.7(3)
C(1)–N(2)–N(1)	105.5(3)	C(4)–N(4)–N(3)	105.8(3)
C(2)–C(1)–N(2)	111.9(4)	C(5)–C(4)–N(4)	112.2(4)
C(3)–C(2)–C(1)	104.1(3)	C(6)–C(5)–C(4)	103.3(3)
C(2)–C(3)–N(1)	109.2(3)	C(5)–C(6)–N(3)	109.9(3)

between a pyrazole and an acetone molecule. The planar cyclopentadienyl ligands adopt an eclipsed conformation, as can be seen on a projection on to the Mo, N(1), O plane (Fig. 3a).

Table 6 lists characteristic molecular dimensions of $[Mo(\eta^5\text{-}C_5H_5)_2LL']$ complexes with ligands coordinated through nitrogen and/or oxygen atoms. The ring normals of **1**, 1.993 and 1.996 Å are in the range of the experimental values quoted from the literature, but the angle between the ring normals, 128.8°, is slightly shorter than the quoted values.

The Mo–O and Mo–N bond lengths 2.026(2) and 2.123(3) Å and the O–Mo–N bond angle 75.4(1)° are similar to the equivalent values observed in the compounds **3**, **4** and **5** in Table 6. It is noteworthy that in all these complexes the metal atom is coordinated to an oxygen and a nitrogen atom of a bidentate ligand. In compounds

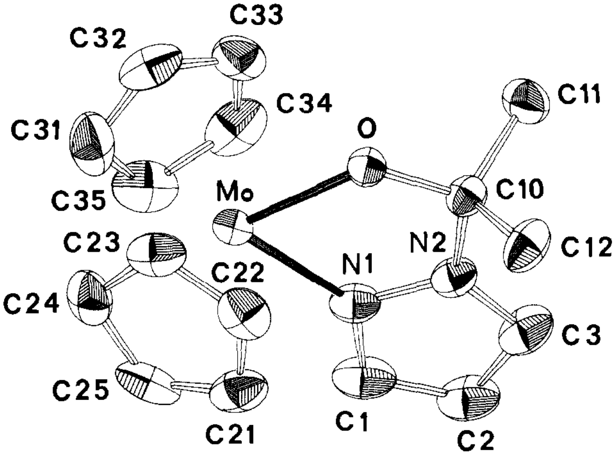

Fig. 1. Molecular structure of $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3C(CH_3)_2O)]^+$ with 30% probability thermal ellipsoids, showing the atom labeling scheme. The hydrogen atoms are omitted.

3, **4** and **5** the presence of hydrogen bonds was considered to be the probable cause for the low value of the O–Mo–N angle compared with the experimental range for the L–Mo–L′ angle, 76–82° observed in other $MoCp_2LL'$ complexes [5]. However, in compound **1** there is no possibility of hydrogen bonding. The presence of two bulky CH_3 groups attached to the tetrahedral carbon atom can impose steric constraints responsible for the low value of the relevant angle. Furthermore, the repulsion between those groups and the Cp rings may also be the cause of the observed decrease in the angle between the ring normals.

The cyclopentadienyl rings are planar with a maximum deviation from the least-squares planes of 0.022 Å. All the atoms of the $N_2C_3H_3C(CH_3)_2O$ ligand, except the CH_3 groups are also in a plane with a maximum deviation from the least-squares plane of 0.024 Å. The angle between the plane defined by the ring normals and the Mo,O,N plane is 89.6°.

Di-η^5-cyclopentadienylbispyrazolatomolybdenum(IV), 2

The crystal structure of **2** consists of discrete $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3)_2]$ molecules at general positions in the unit cell (Fig. 2). The metal atom is coordinated to two η^5-cyclopentadienyl rings and to two nitrogen atoms each of a pyrazolate ligand. The coordination geometry of the ring normals and the nitrogen atoms about the central Mo atom is a distorted tetrahedron.

A projection onto the Mo,N(1), N(3) plane (Fig. 3b) shows that the rings adopt a staggered conformation giving the molecule an approximate C_s symmetry. The molybdenum atom lies at 1.980 and 1.983 Å from the best planes of the cyclopentadienyl rings, and the angle between the ring normals is 133.2°. The Mo–N bond lengths are 2.166(3) and 2.157(3) Å and the N–Mo–N bond angle is 83.3(1)°. This geometry is compared in Table 6 with the corresponding values observed in other di-η^5-cyclopentadienylmolybdenum complexes.

The planar pyrazolate ligands lie in positions (see Fig. 3b) such that a strong repulsion between them is to be expected, leading to the large value of the N–Mo–N

TABLE 6

COMPARISON WITH SIMILAR ($MoCp_2LL'$) COMPLEXES

	$MoCp_2LL'$, ($Cp \equiv \eta^5$-C_5H_5)	Mo-O (Å)	Mo-N (Å)	L-Mo-L′ (deg)	⟨Mo–Cp⟩ [a] (Å)	Cp–Mo–Cp′ (deg) [b]	Ref.
1	$[MoCp_2(N_2C_3H_3C(CH_3)_2O)](PF_6)$	2.026(2)	2.123(3)	75.4(1)	1.995	128.8	This work
2	$[MoCp_2(N_2C_3H_3)_2]$		2.166(3) 2.157(3)	83.3(1)	1.982	133.2	This work
3	$[MoCp_2NH_2CH_2COO]^+ Cl^- \cdot H_2O$	2.10(1)	2.26(1)	74.1(5)	1.990	132.2	7
4	$[MoCp_2NH(CH_3)CH_2COO]^+ Cl^- \cdot CH_3OH$	2.10(2)	2.23(2)	73.4(6)	1.977	133.9	7
5	$[MoCp_2(OH)(NH_2CH_3)](PF_6)$	2.050(5)	2.188(6)	72.2(2)	1.95	133.1	5
6	$[MoCp_2S(CH_2)_2NH_2]^+ I^-$		2.211(15)	78.4(4)	1.989	130.9	6
7	$[MoCp_2NH_2CH(CH_2S)COO]_2H^+ Cl^-$		2.256(7)	77.0(2)	1.980	133.7	7
8	$[MoCp_2NH_2CH(CH_2S)COO]_2H^+(PF_6)^-$		2.14(3)	80(1)	2.01	130	7
			2.32(3)	78(1)	1.98	133	7
9	$\{MoCp_2(NH_3)[HNC(CH_3)(C_2H_5)]\}(PF_6)_2$		2.216(6) 2.192(5)	79.1(2)	1.980	134	8

[a] Average ring normal. [b] Angle between the ring normals.

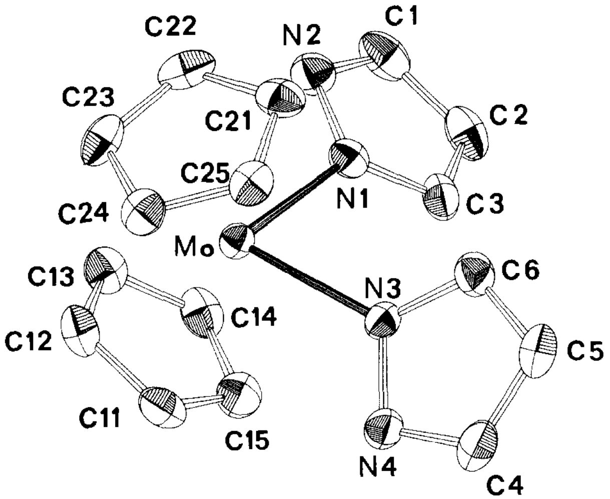

Fig. 2. Molecular structure of $[Mo(\eta^5\text{-}C_5H_5)_2(N_2C_3H_3)_2]$, **2**, with 30% probability thermal ellipsoids, showing the atom labeling scheme. The hydrogen atoms are omitted.

angle. That geometry also seems to minimize the repulsion between those ligands and the Cp rings, yielding an angle between the ring normals in the usual range. The pyrazolate and the cyclopentadienyl ligands are planar, with maximum deviations from the best least-squares planes of 0.008 and 0.013 Å, respectively. The plane defined by the ring normals is perpendicular (90.07°) to the plane defined by the Mo,N(1),N(3) atoms.

Calhorda and Dias [1] tried to prepare binuclear complexes using this bispyrazo-

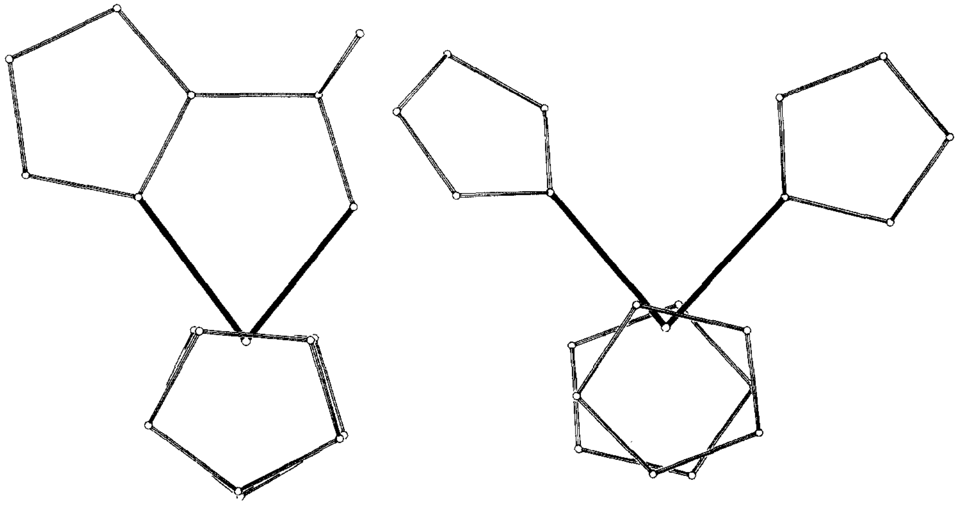

Fig. 3. (a) Projection of the cation of compound **1** on the Mo,N(1),O plane. (b) Projection of the molecule of **2** on to the Mo,N(1),N(3) plane.

late derivative as a ligand. However, to act as a bidentate ligand the N(2) and N(4) nitrogen atoms would have to occupy the C(3) and C(6) carbon positions respectively (see Fig. 2). The thermal parameters of these atoms (see Table 3 and Structure analysis) strongly support the positions of the carbon and nitrogen atoms described here. This structural evidence and the failure to prepare binuclear complexes suggest that the molecular structure of **2** is maintained in solution, and the production of binuclear compounds is thus not practicable.

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