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Synthesis and structural characterization of two molybdenum carbonyl complexes containing dithiocarbamato ligands derived from pyrrolidine and piperidine

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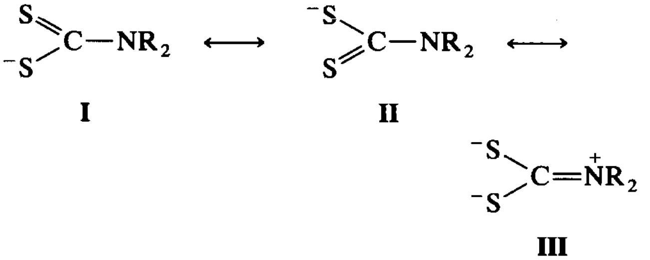
Abstract

Reaction of [Mo(pip)$_2$(CO)$_4$] (pip = piperidine) with (S, S)$^-$ in acetonitrile gives readily [Mo(η^2-(S, S))(CO)$_4$]$^-$, isolated as [PPN][Mo(η^2-(S, S))(CO)$_4$] (PPN$^+$ = bis(triphenylphosphine)iminium; (S, S)$^-$ = pyrrolidine- (**1**) or piperidine-1-carbodithioato (**2**)). The two compounds have been characterized by elemental analysis, IR, nuclear magnetic resonance and X-ray crystallography. **1**: monoclinic, $P2_1/n$; $a = 16.207(5)$, $b = 12.804(3)$ Å, $c = 20.398(4)$ Å; $\beta = 91.02(2)°$; $V = 4232(2)$ Å^3, $Z = 4$; $R = 0.034$, $R_w = 0.037$ based on 4989 reflections with $I > 3.0\sigma(I)$. **2**: monoclinic, $P2_1/n$; $a = 14.148(4)$ Å, $b = 13.646(5)$ Å, $c = 22.535(8)$ Å; $\beta = 95.92(3)°$; $V = 4327(3)$ Å^3, $Z = 4$; $R = 0.054$, $R_w = 0.041$ based on 2048 reflections with $I > 2.0\sigma(I)$. No appreciably modified ligand structure is found in response to the different pK_a of the amine used to form the specific (S, S)$^-$ in the compounds. This feature is rationalized by the electron-withdrawing effect of the metal carbonyl fragment, leading to the observed similarity in both the C–O stretching and the Mo–C–O distances.

1. Introduction

Recently, we have been interested in exploring the sigma donicity of multidentate ligands [1]. We hope that such efforts can lead to more understanding in delineating the kinetics and thermodynamics of organometallic reactions.

The relative contributions of the three canonical forms, **I–III**, depicted below for the dithiocarbamato ligand (S, S)$^-$, have been known to determine the sigma donicity of this ligand [2]. Thus one would expect naturally that, the more basic the amine is used, the more electron donating the dithiocarbamato ligand thus obtained should be. However, we wish to show that the expectation is not reflected in the observed carbonyl stretching bands of the ligated carbonyl complexes of molybdenum(0), although many reports in the literature concerning the sigma donicity of some ligand L in [Mo(CO)$_x$L$_{6-x}$] (x = 1, 2 or 3) match perfectly such an expectation (see for example ref. 3). Apparently, when other counteracting factors are present in the compounds, the observed ν_{CO} values are not necessarily the direct response to the pK_a of the different amine used. Thus, we should be more cautious before proceeding with any prediction or deduction based on the sole feature of organic compounds such as the basicity of the amines.



I **II** **III**

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2. Experimental details

All manipulations were carried out under an atmosphere of pre-purified dinitrogen using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent (ethers, paraffins and arenes from potassium with benzophenone as indicator; halocarbons and acetonitrile from CaH$_2$ and alcohols from the corresponding alkoxide).

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-200 NMR spectrometer and calibrated against internal MeSi$_4$ (TMS) or the deuterated solvent (s, singlet; d, doublet; m, multiplet; br, broad). IR spectra were recorded using a Hitachi 270-30 instrument (vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder). Elemental analysis results were obtained by the staff of the Microanalytical Service, Department of Chemistry, National Cheng Kung University. [Et$_4$N][Mo(η^2-Et$_2$NCS$_2$)(CO)$_4$] was prepared by the published procedure [4] and exhibits four carbonyl-stretching bands at 1998m, 1872s, 1830s, 1788s cm^{-1} in a KBr disc and 2004m, 1880s, 1840s, 1796s cm^{-1} in CH$_2$Cl$_2$.

2.1. Synthesis of [PPN][Mo(η^2-$C_4H_8NCS_2$)(CO)$_4$] (1)

To a 50 ml round-bottomed flask containing a magnetic bar, 0.91 g of [Mo(pip)$_2$(CO)$_4$] (2.42 mmol), 0.43 g of NH$_4^+$C$_4$H$_8$NCS$_2^-$ (2.61 mmol) and 1.43 g of PPN$^+$Cl$^-$ (2.49 mmol) were added with 10 ml of MeCN, where pip represents piperidine and PPN$^+$ is the bis(triphenylphosphine)iminium cation. The resultant solution was stirred for 10 min at room temperature and the solvent was then removed under vacuum to give an orange–yellow solid residue. The solid was washed twice with 5 ml of MeOH to remove excess NH$_4^+$C$_4$H$_5$NCS$_2^-$ and PPN$^+$Cl$^-$ and dried under vacuum to give the pure product (2.12 g, 88%). Anal. Found: C, 60.21; H, 4.30; N, 3.27. C$_{45}$H$_{38}$MoN$_2$O$_4$P$_2$S$_2$ calc.: C, 60.53; H, 4.29; N, 3.14%. ^{1}H NMR (CDCl$_3$,

TABLE 1. Crystal data for the molybdenum(0) dithiocarbamato complexes

Compound	1	2
Empirical formula	$C_{45}H_{38}MoN_2O_4P_2S_2$	$C_{46}H_{40}MoN_2O_4P_2S_2$
Colour	Yellow	Yellow
Crystal size (mm × mm × mm)	0.72 × 0.68 × 0.62	0.20 × 0.20 × 0.15
Space group	Monoclinic, $P2_1/n$ (No. 14)	
Unit-cell dimensions		
a (Å), b (Å), c (Å)	16.207(5), 12.804(3), 20.398(4)	14.148(4), 13.646(5), 22.535(8)
β (°)	91.01(2)	95.92(3)
Volume (Å^3)	4232(2)	4327.3(25)
Z	4	4
D_{calc} (g cm^{-3})	1.401	1.392
Orientation reflections; range	18, 11° $\leqslant 2\theta \leqslant$ 25°	24; 19° $\leqslant 2\theta \leqslant$ 23°
Data collected	$\pm h, +k, +l$	$\pm h, +, +l$
Absorption correction method	ψ scan	
Absorption coefficient (mm^{-1})	0.514	0.50
Absorption correction	Applied	Applied
Transmission range	0.86–0.88	0.947–0.998
Diffractometer used	Siemens R3m/V	Nonius CAD4
Radiation; λ (Å)	Mo Kα; 0.7107	Mo Kα; 0.7093
Temperature (K)	295	298
Scan type	θ–2θ	
2θ range (°)	2–50	2–45
Scan speed (° min^{-1})	3–15	2–8
Standard reflections	3 standard, 50 reflections	Every 7200 s
Decay (%)	$\leqslant 1$	$\leqslant 4$
Number of unique reflections	7515	5634
Number N_o of reflections used	4989 with $I > 3.0\sigma(I)$	2048 with $I > 2.0\sigma(I)$
Number N_v of parameters	658	335
Maximum Δ/σ ratio	0.001	0.193
R; Rw; S [a]	0.034; 0.037; 1.39	0.054; 0.041; 1.39
Weighting factor g [b]	0.0006	0
Residual peak/hole density (electrons Å^{-3})	0.28/ − 0.25	0.31/ − 0.33
Solution	Direct method	Patterson synthesis

[a] $S = [\Sigma|F_o - F_c|^2/(N_o - N_v)]^{1/2}$.

[b] $w^{-1} = \sigma^2(F_o) + g(F_o)^2$.

25°C, 200 MHz): phenyl protons, 7.66 (m, 6H), 7.45 (m, 24H) ppm; pyrrolidine protons, 3.66 (m, 4H), 1.86 (m, 4H) ppm. IR (Kbr): ν_{CO} 1998m, 1870s, 1830s, 1802s; ν_{CN} (assignment tentative in the absence of ^{15}N labelling data) 1462w cm^{-1}. IR(CH_2Cl_2): ν_{CO} 2004m, 1878vs, 1844s, 1798s cm^{-1}.

2.2. *Synthesis of [PPN][Mo(η^2-$C_5H_{10}NCS_2$)(CO)$_4$] (2)*

A mixture of [Mo(pip)$_2$(CO)$_4$] (0.54 g, 1.43 mmol) and 0.43 g of $PPN^+C_5H_{10}NCS_2^-$ (1.08 g, 1.54 mmol) in 10 ml of MeCN was stirred for 10 min at room temperature. The solvent was then removed under vacuum to give an orange–yellow solid residue. The solid was washed twice with 5 ml of MeOH and dried under vacuum to give the pure product (1.28 g; 91%). Anal. Found: C, 60.78; H, 4.46; N, 3.13. $C_{46}H_{40}MoN_2O_4P_2S_2$ calc.: C, 60.93; H, 4.45; N, 3.09%. ^1H NMR ($CDCl_3$, 25°C, 200 MHz): phenyl protons, 7.67 (m, 6H), 7.47 (m, 24H) ppm; piperidine protons, 4.00 (m, 5H), 1.73 (m, 5H) ppm. IR (KBr): ν_{CO} 2000 m, 1872s, 1838s, 1798s cm^{-1}; ν_{CN} (assignment tentative in the absence of ^{15}N labelling data) 1472w cm^{-1}. IR (CH_2Cl_2): ν_{CO} 2004m, 1880vs, 1844s, 1798s cm^{-1}.

2.3. *X-Ray diffraction study of 1 and 2*

All the single crystals were grown from CH_2Cl_2–hexane at room temperature. General procedures and listings of programs were given previously [6]. Absorption correction was performed on the structures using ψ scans. Although all the non-hydrogen atoms were refined anisotropically in **1**, only the non-hydrogen atoms in the anion **2**$^-$ and two P atoms in PPN$^+$ were refined anisotropically in order to keep an optimum ratio between the refined parameters and number of diffraction data used for **2**. The ORTEP plots with the atomic numbering schemes for the anions **1**$^-$ and **2**$^-$ are shown in Figs. 1 and 2 respectively. The related crystal data (Table 1), final coordinates of the non-hydrogen atoms (Tables 2 and 3) and selected bond lengths and angles, (Table 4) are reported. The complete bond lengths and angles, the torsional angles of the pyrrolidine and piperidine rings, the anisotropic displacement coefficients of the atoms, the H atom coordinates and the structural factors are available from the authors.

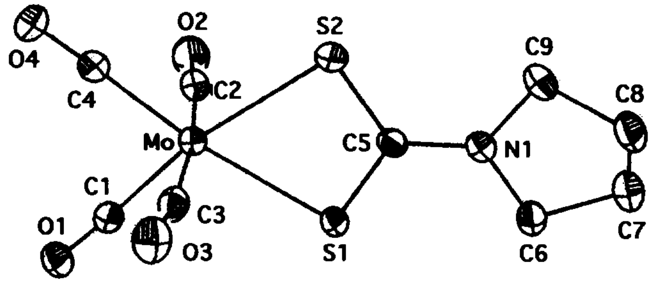

Fig. 1. ORTEP drawing of the [Mo(η^2-$C_4H_8NCS_2$)(CO)$_4$]$^-$ (1$^-$) anion. Thermal ellipsoids are drawn at the 50% probability level.

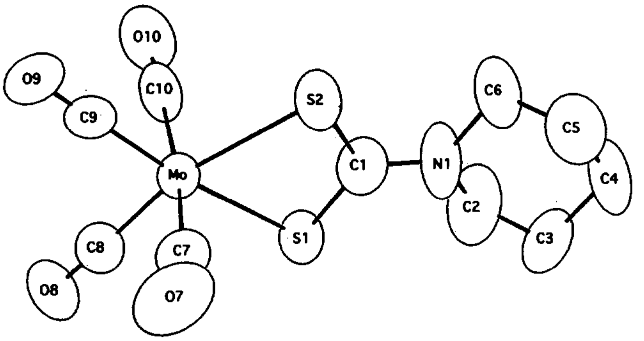

Fig. 2. ORTEP drawing of the [Mo(η^2-$C_5H_{10}NCS_2$)(CO)$_4$]$^-$ (2$^-$) anion. Thermal ellipsoids are drawn at the 50% probability level.

3. Results and discussion

Although the preparation of the molybdenum(0) dithiocarbamato complexes [PPN][Mo(η^2-(S, S))(CO)$_4$] (PPN$^+$ = bis(triphenylphosphine)iminium; (S, S)$^-$ = pyrrolidine- (**1**) or piperidine-1-carbodithioato (**2**)) seems straightforward by simple substitution of carbonyls with the dithiocarbamato ligand (S, S)$^-$, heating the reaction mixture of [Mo(CO)$_6$] and M$^+$(S, S)$^-$ (M$^+$ = Na$^+$ or NH_4^+) in acetonitrile, by following a similar procedure for the synthesis of [Et_4N][Mo(η^2-Et_2NCS_2)(CO)$_4$] (**3**) [4], usually gives untraceable oily products, probably owing to the decomposition of the reactants or product. Like **3**, the air sensitivities of **1** and **2** then make purification of the desired products rather difficult. (As shown previously [4], oxidation of **3** can give the different products [Mo(η^2-(Et_2NCS_2))$_2$(CO)$_2$], [MoO(η^2-(Et_2NCS_2))$_2$], [Mo_2O_3(η^2-(Et_2NCS_2))$_4$] and [Mo_2O_4(η^2-(Et_2NCS_2))$_2$]. It is hence not surprising that some other reports even describe the molybdenum(0) dithiocarbamato complexes (*e.g.* **1**) as unstable or non-isolable [7].) Alternatively, we found that displacement of piperidine (pip) in [Mo(pip)$_2$(CO)$_4$] by (S, S)$^-$ can take place readily in acetonitrile at room temperature and a clean and high yield product can be obtained. Compounds **1** and **2** are soluble in CH_2Cl_2, acetone and acetonitrile, but slightly soluble in Et_2O and MeOH. Although both compounds can be handled for a short period of time in air in the solid state, they are better stored under N_2 at 4°C.

Since piperidine, a six-membered cyclic amine with pK_a = 11.1 [8a], is more basic than pyrrolidine, a five-membered cyclic amine with pK_a = 10.4 [8b,c,9], one

TABLE 2. The fractional atomic coordinates ($\times 10^4$) and U_{eq} ($\times 10^2$)[a] for **1**

Atom	x	y	z	U_{eq}
Mo	2892(1)	6940(1)	689(1)	53(1)
S(1)	3519(1)	8810(1)	683(1)	57(1)
S(2)	2727(1)	7904(1)	1818(1)	64(1)
P(1)	1537(1)	2415(1)	-1149(1)	42(1)
P(2)	3331(1)	2010(1)	-1391(1)	41(1)
O(1)	3296(2)	6137(2)	-705(2)	75(1)
O(2)	1173(2)	7661(3)	85(2)	96(2)
O(3)	4568(2)	5831(3)	1114(2)	87(1)
O(4)	2090(2)	4764(3)	899(2)	94(1)
N(1)	3419(2)	9794(3)	1816(2)	57(1)
N(2)	2422(2)	2439(3)	-1452(2)	52(1)
C(1)	3151(3)	6450(3)	-186(2)	56(1)
C(2)	1796(3)	7429(3)	326(2)	64(2)
C(3)	3982(3)	6290(3)	986(2)	60(2)
C(4)	2376(3)	5587(4)	830(2)	65(2)
C(5)	3237(2)	8943(3)	1480(2)	49(1)
C(6)	3857(4)	10680(4)	1532(3)	67(2)
C(7)	3861(5)	11499(5)	2072(3)	87(2)
C(8)	3817(4)	10876(4)	2684(3)	82(2)
C(9)	3260(4)	9954(5)	2514(2)	74(2)
C(10)	1165(2)	3740(3)	-1088(2)	45(1)
C(11)	1643(3)	4561(3)	-1281(3)	66(2)
C(12)	1337(5)	5578(4)	-1231(3)	85(3)
C(13)	574(4)	5760(4)	-1008(3)	85(2)
C(14)	95(4)	4959(5)	-819(3)	86(2)
C(15)	384(3)	3939(4)	-846(3)	68(2)
C(16)	1476(2)	1865(30	-340(2)	48(1)
C(17)	1269(3)	838(3)	-233(3)	66(2)
C(18)	1332(4)	419(5)	399(3)	83(2)
C(19)	1590(4)	1034(6)	904(3)	90(3)
C(20)	1783(3)	2058(5)	811(3)	83(2)
C(21)	1731(3)	2471(4)	188(2)	66(2)
C(22)	843(2)	1708(3)	-1687(2)	45(1)
C(23)	16(3)	1591(3)	-1544(3)	65(2)
C(24)	-518(3)	1116(4)	-1989(3)	76(2)
C(25)	-226(4)	738(4)	-2558(3)	76(2)
C(26)	587(4)	829(4)	-2705(3)	74(2)
C(27)	1136(3)	1314(3)	-2272(2)	56(1)
C(28)	3831(2)	2400(3)	-642(2)	47(1)
C(29)	4403(3)	1777(4)	-318(2)	56(1)
C(30)	4794(3)	2139(5)	251(2)	74(2)
C(31)	4602(3)	3107(5)	489(3)	84(2)
C(32)	4046(4)	3722(5)	170(3)	99(3)
C(33)	3657(3)	3381(4)	-397(3)	74(2)
C(34)	3411(2)	615(3)	-1450(2)	43(1)
C(35)	3738(3)	120(3)	-1995(2)	57(1)
C(36)	3772(3)	-953(3)	-2030(2)	66(2)
C(37)	3482(3)	-1548(3)	-1529(2)	61(2)
C(38)	3145(3)	-1079(3)	-991(2)	59(2)
C(39)	3113(3)	-1(3)	-947(2)	52(1)
C(40)	3886(2)	2542(3)	-2070(2)	44(1)
C(41)	3467(3)	3039(3)	-2575(2)	53(1)
C(42)	3880(3)	3412(4)	-3111(2)	66(2)
C(43)	4722(3)	3285(4)	-3149(2)	68(2)
C(44)	5150(3)	2794(4)	-2649(2)	65(2)
C(45)	4740(3)	2424(3)	-2110(2)	54(1)

[a] U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. The fractional atomic coordinates and B_{eq}[a] for **2**

Atom	x	y	z	B_{eq} (Å^2)
Mo	0.23499(11)	0.18988(11)	0.02725(7)	4.23(8)
S(1)	0.2153(3)	0.2079(3)	0.14009(20)	5.5(3)
S(2)	0.1967(4)	0.0241(3)	0.07607(21)	5.9(3)
C(1)	0.1910(13)	0.0846(12)	0.1411(7)	6.3(11)
N(1)	0.1675(12)	0.0404(10)	0.1908(6)	8.3(10)
C(2)	0.1490(16)	0.0908(14)	0.2452(8)	10.2(16)
C(3)	0.1953(16)	0.0492(14)	0.2969(8)	9.5(15)
C(4)	0.1686(15)	-0.0590(14)	0.3003(8)	9.2(14)
C(5)	0.1877(14)	-0.1093(14)	0.2452(9)	9.1(14)
C(6)	0.1400(16)	-0.0669(13)	0.1914(9)	9.7(15)
C(7)	0.3751(11)	0.1645(12)	0.0373(7)	5.7(10)
O(7)	0.4544(8)	0.1511(11)	0.0333(5)	10.1(10)
C(8)	0.2627(11)	0.3268(12)	0.0127(7)	5.2(10)
O(8)	0.2789(8)	0.4093(8)	0.0038(5)	7.0(7)
C(9)	0.2451(11)	0.1617(12)	-0.0561(7)	5.2(9)
O(9)	0.2485(8)	0.1448(9)	-0.1060(5)	7.9(8)
C(10)	0.0965(11)	0.2070(12)	0.0017(7)	5.7(10)
O(10)	0.0166(8)	0.2088(10)	-0.0190(6)	9.2(6)
N(2)	0.2221(8)	0.6035(8)	0.8123(5)	3.3(6)
P(1)	0.3190(3)	0.6371(3)	0.84743(17)	3.07(20)
P(2)	0.1149(3)	0.6383(3)	0.81054(18)	3.23(21)
C(11A)	0.3857(9)	0.5292(10)	0.8700(6)	2.9(3)
C(12A)	0.4716(10)	0.5391(11)	0.9067(6)	3.9(4)
C(13A)	0.5222(12)	0.4568(12)	0.9286(7)	5.6(4)
C(14A)	0.4851(10)	0.3656(11)	0.9122(7)	4.5(4)
C(15A)	0.4020(11)	0.3538(12)	0.8767(7)	5.0(4)
C(16A)	0.3512(10)	0.4358(11)	0.8556(6)	4.0(4)
C(11B)	0.3062(9)	0.7033(10)	0.9146(6)	3.0(3)
C(12B)	0.3096(10)	0.8058(12)	0.9165(6)	4.1(4)
C(13B)	0.2881(10)	0.8524(11)	0.9688(7)	4.6(4)
C(14B)	0.2676(10)	0.7996(12)	1.0173(6)	4.5(4)
C(15B)	0.2650(10)	0.6993(12)	1.0152(6)	4.6(4)
C(16B)	0.2846(10)	0.6516(10)	0.9636(6)	3.9(4)
C(11C)	0.3879(9)	0.7111(10)	0.8005(6)	3.6(4)
C(12C)	0.3571(10)	0.7140(11)	0.7390(6)	4.6(4)
C(13C)	0.4106(11)	0.7700(12)	0.7043(7)	5.7(5)
C(14C)	0.4903(11)	0.8175(13)	0.7279(7)	5.5(4)
C(15C)	0.5203(11)	0.8155(13)	0.7860(7)	5.8(4)
C(16C)	0.4684(10)	0.7591(12)	0.8232(6)	4.4(4)
C(21A)	0.0532(9)	0.5640(10)	0.8597(6)	2.9(3)
C(22A)	0.1012(10)	0.4902(11)	0.8929(6)	3.7(4)
C(23A)	0.0513(10)	0.4315(12)	0.9291(7)	4.7(4)
C(24A)	-0.0423(11)	0.4482(12)	0.9338(7)	5.6(4)
C(25A)	-0.0921(11)	0.5206(12)	0.9025(7)	5.1(4)
C(26A)	-0.0431(10)	0.5802(11)	0.8665(6)	4.1(4)
C(21B)	0.0593(9)	0.6204(10)	0.7367(6)	3.1(3)
C(22B)	-0.0294(11)	0.6631(11)	0.7189(7)	5.0(40
C(23B)	-0.0737(11)	0.6454(12)	0.6629(7)	5.8(5)
C(24B)	-0.0351(11)	0.5844(12)	0.6255(7)	5.3(4)
C(25B)	0.0496(12)	0.5444(13)	0.6408(7)	6.2(5)
C(26B)	0.0983(11)	0.5609(11)	0.6972(7)	4.5(4)
C(21C)	0.1008(9)	0.7657(10)	0.8284(6)	2.9(3)
C(22C)	0.1338(10)	0.8354(11)	0.7903(6)	4.1(4)
C(23C)	0.1307(11)	0.9338(12)	0.8047(7)	5.2(4)
C(24C)	0.0963(11)	0.9611(11)	0.8569(7)	4.6(4)
C(25C)	0.0641(11)	0.8950(12)	0.8955(7)	5.3(4)
C(26C)	0.0669(10)	0.7944(12)	0.8809(6)	4.7(4)

[a] B_{eq} is the mean of the principal of the thermal ellipsoid.

would expect that the related dithiocarbamato ligand, $C_5H_{10}NCS_2^-$, should be more electron donating than the other, $C_4H_8NCS_2^-$, in [PPN][Mo(η^2-(S, S))(CO)$_4$]. The IR bands, tentatively assigned to ν_{CN} of 1462 cm^{-1} for [PPN][Mo(η^2-$C_4H_8NCS_2$)(CO)$_4$]. (**1**) and 1472 cm^{-1} for [PPN][Mo(η^2-$C_5H_{10}NCS_2$)(CO)$_4$]. (**2**) in KBr, seems compatible with the presence of the more canonical form **III** in **2** than in **1**, but this assignment is subject to confirmation by ^{15}N labelling studies. (Although the ν_{CN} bands assigned to the binary compounds of transition metal atoms in high oxidation states such as [Nb(η^2-Et_2NCS_2)$_3$Cl] [10,11] are usually observed with a strong or very strong intensity, the bands in the dithiocarbamato-ligated carbonyl complexes of molybdenum(0) are found to have a weak intensity, which may overlap with bands for either C–H bending or phenyl-ring stretching vibration [12].) Surprisingly, the two sets of the four IR-active carbonyl-stretching bands, measured in CH_2Cl_2 or in KBr, are similar to each other for complexes **1** and **2** (and similar to the bands for **3**) in the expected C_s symmetry. Since we just reported the correlation between the unexpected ν_{CO} bands and the modified coordination structure [13], the feature observed in **1–3** can also be possibly attributed into the structural effect, in which the sulphur-bidentate ligand (S, S)$^-$ may coordinate inequivalently with the central metal atom to reflect respective bulk of the different alkyl substituents on the nitrogen atom of the ligand.

In order to confirm this explanation, we determined the crystal structures of **1** and **2** compared with that of [Et_4N][Mo(η^2-Et_2NCS_2)(CO)$_4$] (**3**) [6] or that of [PPN][Mo(η^2-Et_2NCS_2)(CO)$_4$] (**4**) [14]. As shown in Figs. 1 and 2 and Table 4, the geometry of the anion **1**$^-$ or **2**$^-$ is pseudo-octahedral with a small S–Mo–S angle of 67.5(1)° in **1**$^-$ and 67.66(16)° in **2** and is quite similar to that of **3**$^-$ (S–Mo–S angle, 67.7(2)° [6]) or that of **4**$^-$ (S–Mo–S angle, 67.82(5)° [14]). The C–N bond lengths of 1.319(5) Å in **1**, 1.344(22) Å in **2**, 1.329(13) Å in **3** and 1.343(7) Å in **4** are also similar to each other within the experimental errors. Since structure **4** has a crystallographically imposed twofold axis, through the Mo atom and the C–N bond of the dithiocarbamato group, the group is a perfect equivalent bidentate ligand with an Mo–S bond length of 2.5963(13) Å, very close to the average value of 2.593 Å from the two apparently different Mo–S bond lengths of 2.607(3) and 2.578(4) Å in **3**. This comparison shows that a difference between the two bond lengths as large as 0.03 Å can still be attributed into the crystal packing effect [14,15] and the group should be regarded as an equivalent bidentate ligand in this structure. Accordingly, the pyrrolidine-1-carbodithioato group in **1** with Mo–S bond lengths of 2.631(1) and 2.600(1) Å or the piperidine-1-carbodithioato group in **2** with Mo–S bond lengths of 2.597(5) and 2.598(5) Å (Table 3) can also be considered as equivalent. (This argument seems evident, for the relative Mo–C–O and C–O bond lengths

TABLE 4. Selected bond lengths and angles for **1** and **2**

	Bond length (Å)		Bond length (Å)		Bond angle (°)		Bond angle (°)
Compound **1**							
Mo–S(1)	2.600(1)	Mo–S(2)	2.631(1)	S(1)–Mo–S(2)	67.5(1)	C(1)–Mo–C(4)	87.0(2)
Mo–C(1)	1.944(4)	Mo–C(2)	2.013(5)	C(2)–Mo–C(3)	173.1(2)	S(1)–C(5)–S(2)	116.4(2)
Mo–C(3)	2.035(5)	Mo–C(4)	1.947(5)	Mo–S(1)–C(5)	88.6(1)	Mo–S(2)–C(5)	87.4(1)
S(1)–C(5)	1.704(4)	S(2)–C(5)	1.716(4)	N(1)–C(6)–C(7)	104.0(4)	C(6)–C(7)–C(8)	103.8(4)
C(1)–O(1)	1.160(5)	C(2)–O(2)	1.154(6)	C(7)–C(8)–C(9)	105.3(5)	C(8)–C(9)–N(1)	102.4
C(3)–O(3)	1.143(6)	C(4)–O(4)	1.161(6)	C(9)–N(1)–C(6)	111.8(4)		
C(5)–N(1)	1.319(5)	N(1)–C(6)	1.464(6)				
C(6)–C(7)	1.522(8)	C(7)–C(8)	1.483(8)				
C(8)–C(9)	1.522(8)	C(9)–N(1)	1.466(6)				
Compound **2**							
Mo–S(1)	2.598(5)	Mo–S(2)	2.597(5)	S(1)–Mo–S(2)	67.66(15)	C(8)–Mo–C(9)	89.5(6)
Mo–C(7)	2.002(16)	Mo–C(8)	1.943(17)	C(7)–Mo–C(10)	169.4(7)	S(1)–C(1)–S(2)	116.1(10)
Mo–C(9)	1.937(15)	Mo–C(10)	1.999(16)	Mo–S(1)–C(1)	87.8(6)	Mo–S(2)–C(1)	88.4(6)
S(1)–C(1)	1.718(17)	S(2)–C(1)	1.690(17)	N(1)–C(2)–C(3)	113.7(16)	C(2)–C(3)–C(4)	109.7(17)
C(7)–O(7)	1.150(20)	C(8)–O(8)	1.170(20)	C(3)–C(4)–C(5)	109.2(15)	C(4)–C(5)–C(6)	113.8(17)
C(9)–O(9)	1.153(18)	C(10)–O(10)	1.177(20)	C(5)–C(6)–N(1)	107.8(16)	C(6)–N(1)–C(2)	112.4(15)
C(1)–N(1)	1.344(22)	N(1)–C(2)	1.454(24)				
C(2)–C(3)	1.40(3)	C(3)–C(4)	1.53(3)				
C(4)–C(5)	1.52(3)	C(5)–C(6)	1.40(3)				
C(6)–N(1)	1.514(23)						

and the associated angles in **1–4** are very similar within the experimental errors, also explaining the similarity in the observed carbonyl-stretching bands.) Obviously, there is not any appreciably modified ligand structure in response to the different pK_a of the amine used to form the specific (S, S)$^-$ in the compounds [16]. This feature probably reflects that the similarity in both the C–O stretching and the Mo–C–O distances is not related in a simple direct way to the amine used in (S, S)$^-$ for **1–3**. We would suggest that the synergistic mechanism [17] between Mo and carbonyls in the compounds is ready to dissipate any accumulated electron density resulting from the coordination of (S, S)$^-$ and allows the higher possible electron donation of the dithiocarbamato group in the compounds so that the group is eventually forced to take the canonical form **III**. In other words, it is possible that the electron-withdrawing effect of the metal carbonyl fragment determines the observed spectral and structural features.

By comparing the torsional angles, the five-membered ring in **1** is closed to a skew-boat geometry while the six-membered ring in **2** is in a chair form [18]. The associated bond lengths and angles in these rings are quite similar to those reported for [M(S, S)$_2$] (M = Ni or Cu; (S, S) = $C_4H_8NCS_2^-$ [19] or $C_5H_{10}NCS_2^-$ [20]). Apparently, the distance between the cyclic ring and the metal core in **1** or **2** is quite long and no mutual steric influence in the related bond parameters can be observed.

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