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Tris(dialkyldithiocarbamato)diazenido(1-) and hydrazido(2-) molybdenum complexes: synthesis and reactivity in acid medium

Pablo C. Riveros^a, Isabel C. Perilla^a, Arnulfo Poveda^{a,*}, Heimo J. Keller^b, H. Pritzkow^b

^a Departamento de Química, Universidad Nacional de Colombia, Santafé de Bogota, Colombia ^b Anorganisch-Chemiches Institut der Universität, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

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Abstract

A series of new molybdenum complexes, $[Mo(NNH-CO-Ph){S_2CN(C_2H_5)_2}_3]$ (1), $[Mo(NN-CO-C_6H_4-NO_2){S_2CN(C_2H_5)_2}_3]$ (2), $[Mo(NNH-CO-Ph){S_2CN(CH_3)_2}_3]$ (3), $[Mo(NN-CO-C_6H_4-NO_2){S_2CN(CH_3)_2}_3]$ (4) have been synthesized, with *p*-ni-trobenzoyldiazenido(1-) and benzoyldydrazido(2-) as ligands, and dialkyldithio-carbamatos as coligands. Reactions of these compounds with aqueous and methanolic HCl were carried out but the attempted separation of the aroyl group was unsuccessful. Only the reaction of 1 and 2 with HCl in methanol gave a product, identified as $[Mo{S_2CN(C_2H_5)_2}_4][MoCl_4(OCH_3)_2]$. The complexes were characterized by elemental analysis, IR spectroscopy, ¹H and ¹³C NMR, and mass spectrometry. Single crystals of 2 were obtained and the crystal structure was determined. The Mo atom is heptacoordinated; one diazenido(1-) and three diethyldithiocarbamatos act as ligands. From the latter one sulfur is in *trans*-position to the diazenido-nitrogen atom and the other five sulfur atoms lie in a plane giving a distorted pentagonal-bipyramidal coordination. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

There have been several recent studies concerning the reactivity of dinitrogen coordinated to transition metal ions. Besides substitution, the reactions that give rise to N_2 derivatives such as hydrazido(2-), (1-), or diazenido(1-) are the most interesting [1–4]. Similar intermediates can be obtained by reaction of hydrazines with dioxomolybdenum complexes; however, there are not many reports in the literature of acyl or aroyl hydrazido or diazenido complexes [5]. These ligands can act as monodentate or didentate and generate derivatives that may be considered as intermediates in a cyclic process of nitrogen fixation, similarly to some rhenium complexes with phosphine ligands [6]. The aroyl and acyl derivatives could also give azido(–NNH)

or hydrazido($-NNH_2$) complexes by breaking the C(O)–N bond in a solvolysis reaction. All aroyl hydrazines used in this work act as monodentate. The aroyl hydrazine derivatives with dimethyldithiocarbamato coligand are stable to solvolysis whereas those with diethyldithiocarbamato react under reflux to give tetra-dithiocarbamato complexes.

2. Experimental

2.1. Physical measurements

Melting points were obtained with a Melt-Temp II apparatus, using glass capillaries. Elemental analyses were performed at the Microanalyses Department of the Anorganisch-Chemischen Institut of Heidelberg Universität. IR spectra were recorded for solid dispersions of 5% samples in KBr by the reflectance technique in a Nicolet 510P FT-IR spectrometer. ¹H and ¹³C NMR spectra were obtained at room temperature (r.t.)

^{*} Corresponding author. Tel.: + 57-1-316-5000, ext. 1443; fax: + 57-1-316-5220.

E-mail address: apovedap@ciencias.ciencias.unal.edu.co (A. Poveda).

in a Brucker Typ AC 300 spectrometer at 300 and 75 MHz respectively, using TMS as standard; CDCl₃ was used as solvent for all samples but [MoO₂{S₂CN- $(CH_3)_2$, which was taken in $(CD_3)_2$ SO. Mass spectra were recorded in a Finnigan Mat 8200 spectrometer using the FAB-Nibeol ionization technique. Small single crystals of 2 were obtained from THF solution. Crystal data were collected at -70° C with a Siemens-Stoe AED2 diffractometer using Mo K α radiation, a graphite monochromator and omega-scan. The structure was solved by direct methods (SHELXS-86) [7]. The compound crystallizes with one half THF per molecule. The THF molecule is disordered. It was not possible to distinguish the oxygen from the carbon atoms, then the solvent molecule was refined for five carbon atoms with restrictions on the bond lengths and angles. The structure was refined by least-squares methods based on F_2 with all measured reflections (SHELXL-97 [8]) using anisotropic temperature factors for all non-hydrogen atoms except those of the THF molecule. Hydrogen atoms were inserted in calculated positions or as part of a rigid group (methyl).

2.2. Synthesis of the dioxocomplexes

2.2.1. Bis(dimethyldithiocarbamato)-

 $dioxomolybdenum(VI), [MoO_2{S_2CN(CH_3)_2}_2]$

A solution of 9.40 g (50 mmol) of NaS₂CN(CH₃)₂· 2.5H₂O in 100 ml H₂O was slowly added to a solution of 8.70 g (7 mmol) of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 100 ml H₂O, with strong stirring. The pH was kept at about 2 by adding 1 M HNO₃. The obtained yellow precipitate was filtered off and washed with water, then dried under vacuum. Yield, 99%. The compound decomposes between 290–300°C. (Elemental analysis: *Anal*. Found: C, 28.13; H, 4.64; N, 6.40. Calc.: C, 28.30; H, 4.75; N, 6.60%).

2.2.2. Bis(diethyldithiocarbamato)dioxomolybdenum(VI), $[MoO_2\{S_2CN(C_2H_5)_2\}_2]$

The previously described procedure was employed, using 10.00 g (44 mmol) of NaS₂CN(C₂H₅)₂·3H₂O in 150 ml H₂O, and 10.00 g (8 mmol) of (NH₄)₆Mo₇O₂₄· 4H₂O in 150 ml H₂O. The yellow compound was recrystallized in 1:1 benzene: n-hexane. Yield, 95%. m.p., 133°C. (Elemental analysis: *Anal.* Found: C, 19.27; H, 3.34; N, 7.62; S, 34.27. Calc.: C, 19.56; H, 3.28; N, 7.60; S, 34.82%).

2.3. Synthesis of the aroylhydrazine derivatives

2.3.1. Benzoylhydrazido(2-)tris(diethyldithiocarbamato)molybdenum(V), $[Mo(NNH-CO-Ph){S_2CN(C_2H_5)_2}_3]$ (1)

A suspension of 1.00 g (2.36 mmol) of $[MoO_2{S_2CN-(C_2H_5)_2}]$, 0.60 g (2.66 mmol) of $NaS_2CN(C_2H_5)_2$.

 $3H_2O$, and 0.60 g (4.4 mmol) of PhCONHNH₂ in 20 ml methanol were boiled under reflux for 2 h with magnetic stirring. Longer times of reflux lead to lower yield, whereas shorter times cause the product to be contaminated with the reactants. The solvent was reduced to about 10 ml in a rotary evaporator and the solution was cooled to r.t. The orange solid thus obtained was filtered and washed with methanol, water, and again with a little methanol. The product was recrystallized in methanol and dried under vacuum. It can also be recrystallized in THF. Yield, 82%. The same product was obtained with 1:0:1 and 1:0:2 molar ratios of reactants respectively, but the yield decreased to 30 and 38%. Elemental analysis: *Anal.* Found: C, 38.31; H, 5.17; N, 10.14. Calc.: C, 39.21; H, 5.24; N, 10.39%.

2.3.2. Tris(diethyldithiocarbamato)-p-nitrobenzoyldiazenido(1-)molybdenum(IV), [$Mo(NNCO-C_6H_4-NO_2)$ { $S_2CN(C_2H_5)_2$ }] (2)

The procedure described above was employed, using 1.00 g (2.35 mmol) of $[MoO_2{S_2CN(C_2H_5)_2}_2]$, 0.60 g (2.66 mmol) of $NaS_2CN(C_2H_5)_2$ '3H₂O, and 0.80 g (4.41 mmol) of $O_2N-C_6H_4CONHNH_2$. The red solid was recrystallized in THF and dried under vacuum for one h at 35°C. Yield, 80%. With 1:0:2 molar ratio of reactants the same product was obtained in 35% yield. (Elemental analysis: *Anal*. Found: C, 38.27; H, 5.22; N, 11.09; S, 25.15. Calc. for $[Mo(NNCO-C_6H_4-NO_2)-{S_2CN(C_2H_5)_2}_3]$ ·0.5THF: C, 38.18; H, 5.07; N, 11.13; S, 25.48%). Crystals for X-ray analysis were grown by dissolving the compound in THF at 20°C and then filtering. The solution was warmed at about 60°C and after 12 h red crystals were obtained.

2.3.3. Benzoylhydrazido(2-)tris(dimethyldithiocarbamato)molybdenum(V),

 $[Mo(NNHCO-Ph)\{S_2CN(CH_3)_2\}_3] (3)$

The procedure as described above was employed, using 1.00 g (2.71 mmol) of $[MoO_2{S_2CN(CH_3)_2}_2]$, 0.55 g (2.92 mmol) of NaS₂CN(CH₃)₂·2.5H₂O, and 0.60 g (4.41 mmol) of Ph–CO–NHNH₂. The product was recrystallized in methanol or THF and dried under vacuum. Yield, 75%. The same product was obtained in 1:0:2 molar ratio of reactants, in 33% yield. (Elemental analysis: *Anal.* Found: C, 32.56; H, 4.10; N, 11.61. Calc: C, 32.59; H, 3.93; N, 11.88%).

2.3.4. Tris(dimethyldithiocarbamato)-pnitrobenzoyldiazenido(1-)molybdenum(IV), $[Mo(NNCO-C_6H_4-NO_2) \{S_2CN(CH_3)_2\}_3]$ (4)

The procedure described above was employed, using 1.50 g (4.07 mmol) of $[MoO_2{S_2CN(CH_3)_2}_2]$, 0.90 g (4.79 mmol) of $NaS_2CN(CH_3)_2\cdot 2.5H_2O$, and 1.20 g (6.63 mmol) of $O_2N-C_6H_4$ -CO-NHNH₂. The product was recrystallized in THF and dried under vacuum. Yield, 81%. The same product was obtained in 30%

yield when a 1:0:2 molar ratio of reactants was used. (Elemental analysis: *Anal*. Found: C, 30.85; H, 3.75; N, 13.10; S, 29.90. Calc.: C, 30.28; H, 3.49; N, 13.24; S, 30.31%).

2.4. Solvolysis of the hydrazido(2-) and diazenido(1-) derivatives

The solvolysis of 1, 2, 3, and 4 was attempted in 5% and 10% NaOH in water and in methanol at r.t. for 24 h but no reaction was observed. The reactants decomposed when refluxed at 60°C for 2 h. The same compounds did not react with 37% HCl in water at r.t. for 24 h, neither with 5% HCl below 50°C. At 60°C decomposition of the reactants was observed. IR spectroscopy was used as a probe to monitor the course of the reactions.

Only the reaction of the diethyldithiocarbamato derivatives 1 and 2 with 2.5% HCl in methanol under reflux gave an identifiable product.

2.5. Tetrakis(diethyldithiocarbamato)molybdenum(V)tetrachlorobis(methoxy) molybdate(V), $[Mo(S_2CN(C_2H_5)_2)_4][MoCl_4(OCH_3)_2]$ (5)

A suspension of 0.30 g of 1 in 15 ml of a solution of concentrated HCl 2.5% v/v in methanol was placed under reflux; after 45 min a green precipitate formed, that was filtered and washed with water, diethyl ether and n-hexane. Its m.p. (143°C) and mass spectra showed it to be the unstable known compound $[Mo{S_2CN(C_2H_5)_2}_4]$ [9]. After refluxing for 2 h, the resultant brown solution was evaporated in a rotary evaporator until about 4 ml, then it was warmed and diethyl ether added drop to drop, until a brown solid precipitated. The solid was filtered and washed at 0°C with diethyl ether and methanol. Then it was recrystallized in methanol and dried under vacuum. Yield, 27%. The product is insoluble in acetone, diethyl ether, chloroform, and dimethyl sulfoxide (Elemental analysis: Anal. Found: C, 26.72; H, 4.69; Cl, 14.34; N, 5.67; S, 25.94; Calc. for $[Mo{S_2CN(C_2H_5)_2}_4][MoCl_4(OCH_3)_2]$: C, 26.80; H, 4.74; Cl, 13.37; N, 6.44; S, 25.63). When 2 was allowed to react by the above described procedure the same products were obtained under the same conditions but in lower yield (5 was formed in 20% yield).

2.6. Tris(diethyldithiocarbamato)acetylhydrazido(2-)molybdenum(V), $[Mo(NNHCO-CH_3){S_2CN(C_2H_5)_2}_3]$.

A suspension of 0.50 g (1.18 mmol) of $[MoO_2{S_2CN}(C_2H_5)_2]_2$, 0.50 g (2.22 mmol) of $NaS_2CN(C_2H_5)_2$. 3H₂O, and 0.22 g (2.97 mmol) of CH₃-CO-NHNH₂ in 15 ml methanol was stirred for 12 h at r.t. The solution thus obtained was filtered and then evaporated until dryness in a rotary evaporator at 48°C. The resultant brown solid was suspended in 50 ml water and stirred for 30 min to dissolve and thus eliminate the excess of reactants. The precipitate was filtered and then washed with water, ethanol, and n-hexane. The product was recrystallized in ethanol; after three days brown microcrystals precipitated, which were filtered and washed with n-hexane, and diethyl ether. The product was dried under vacuum. Yield, 65%. ¹H NMR $\delta_{\rm H}$ (solvent CDCl₃) 1.12–1.35 (18H, m, 6CH₃), 1.95–2.20 (1H, br s, N–H), 2.17 (3H, s, CH₃–CO), 3.65–3.85 (12H, m, 6CH₂).

2.7. Trisdiethyldithiocarbamatophenyldiazenido(1-)molybdenum(IV), $[Mo(NNPh){S_2CN(C_2H_5)_2}_3]$.

This compound was prepared following a published procedure [10].

3. Results and discussion

3.1. Synthesis of the compounds

The dioxocomplexes were synthesized by a modification of the procedure published by Moore and Larson [11]; the pH was kept below 2.0 with diluted HNO₃ in order to avoid contamination with the violet Mo(V) complex, [{Mo(S₂CNR₂)₂O}.

It has been published that the reactivity of dioxocomplexes against substituted hydrazines depends on several factors, such as the nature of the coligands and of the hydrazines, and the molar ratio of the reactants; for example, the number of substituents and the basicity of the hydrazines play an important role in the number of these that coordinate to the metal center [12-15]. In this work we found that condensation reactions between the dioxocomplexes and the hydrazides in the presence of the corresponding dialkyldithiocarbamate in methanol always give tris(dialkyldithiocarbamato) complexes of the type [Mo(NNHCO-Ph)(S₂CNR₂)₃] and $[Mo(NNCO-C_6H_4-NO_2)(S_2CNR_2)_3]$ (R = -CH₃ or $-C_2H_5$). The same compounds are formed when no dialkyldithiocarbamate is added although in lower yield, since the additional dithiocarbamate has to be provided by decomposition of the original dithicarbamato complex.

The acyldiazenido- and acylhydrazido- ligands may be either monodentate when they are bound to the metal through the terminal nitrogen, or didentate when they are bound through the nitrogen and the oxygen. In addition, the monodentate ligand can bind the metal center in three different ways depending on the hydrazide from which it originates, as diazenido(1-), hydrazido(1-), or hydrazido(2-) [12,13]. These binding modes are shown in Fig. 1. In our case the two hydrazides act as monodentate ligands; *p*-nitrobenzohy-



Fig. 1. Types of ligation and binding modes of the hydrazido ligands.

drazide is bound to the metal as diazenido(1-), and benzohydrazide as hydrazido(2-). A plausible explanation for this difference is that when the $-NO_2$ group is present, electron density is withdrawn from the nitrogen atom and therefore the N–H bond is unstable. Then the oxidation state of molybdenum is different with these ligands; it acts as Mo(IV) in diazenido(1-) complexes, and as Mo(V) in hydrazido(2-) complexes. The paramagnetism of the latter was proven by EPR, in which a signal at $g_{av} = 1.980$ is seen.

3.2. Reactivity of p-nitrobenzoyldiazenido(1-) and benzoylhydrazido(2-) complexes with acids and bases in aqueous and methanolic media

Compounds 1 and 3 are neither protonated nor deprotonated on the nitrogens of the diazenido or hydrazido ligands when boiled under reflux with base or acid in methanolic or aqueous medium. On the other hand, the same nitrogen atoms in compounds 2 and 4 are not protonated when reacting with acid in methanol, or in water. When 1 is allowed to react with HCl in methanol (2.5 ml concentrated HCl in 95 ml MeOH) under reflux, a green solid precipitates after 45 min. This precipitate is insoluble in water but soluble in chloroform, dichloromethane and acetone, indicating a non-ionic or slightly polar nature. In the solid state this compound is unstable to air, and even more in solution, and this makes difficult to take NMR spectra. The MS indicates this compound to be $[Mo(dedtc)_{4}]^{1}$, which is confirmed by its m.p., 143°C, similar to that reported in the literature [9]. The same compound was also obtained in 24% yield when 2 was allowed to react by the same procedure.

At longer reaction time (2 h) the oxidation product of $[Mo(dedtc)_4]$, $[Mo\{S_2CN(C_2H_5)_2\}_4][MoCl_4(OCH_3)_2]$ (5) was isolated, being the metal of the cation in the 5 + oxidation state. Similar types of oxidation reactions have already been reported and are used for the synthesis of the cation [9,16]. Several ionic compounds that contain the $[Mo(S_2CN(C_2H_5)_2)_4]^+$ cation have been reported, which have been prepared from $[Mo_2O_2Cl_6]$ and $\{(C_2H_5)_2NH_2\}\{S_2CN(C_2H_5)_2\}$, or by oxidation of the corresponding Mo(IV) compounds [9,16,17]. The presence of the anion $[MoCl_4(OCH_3)_2]^-$ is proposed mainly on the basis of elemental analysis, since the compound is not soluble enough to allow to take NMR spectra; this anion has also been isolated from the reaction between $[Mo_2Cl_{10}]$ and CH_3OH [16].

3.3. IR spectroscopy

As expected, the dialkyldithiocarbamato coligands show IR bands due to the C=N stretching mode between 1540 and 1506 cm⁻¹, indicating a double bond character; bands due to C-S stretching are found between 1010 and 999 cm⁻¹; the C-H stretching for ethyl and methyl groups is shown in the region 2981-2858 cm⁻¹, the C-H bending modes appear as two bands around 1460 and 1380 cm^{-1} in the diethyldithiocarbamato complexes, and as only one band around 1395 cm^{-1} in the dimethyldithiocarbamato complexes [9,11,18]. The *p*-nitrobenzoyldiazenido and benzoylhydrazido ligands show bands for the =C-H stretching of the aromatic ring between 3071 and 3053 cm^{-1} , and also the out-of-plane =C-H bending modes of the aromatic rings around 700 cm⁻¹. Tables 1 and 2 show the positions of some selected bands. Two strong bands in the region 870-915 cm⁻¹ assigned to cis-Mo=O stretchings are present in the dioxocomplexes, but disappear in the benzoylhydrazido- and *p*-nitrobenzoyldiazenidocomplexes, as expected.

The shift of the v(C-O) and v(N-N) IR bands according to the change in the CO bond order allows to determine whether the hydrazido and diazenido ligands act as mono- or didentate. If the IR spectrum shows bands assignable to v(C=O) and v(N=N), the ligand is acting as monodentate; on the other hand, if the v(C=O) band disappears and the v(N=N) band is

Table 1								
Selected	IR	bands	for	the	hidrazido	and	diazenido	ligands

			-	
Complex	v(=C–H)	$\delta(=\!\!C\!\!-\!\!H)^{\rm a}$	v(C=O)	v(N=N)
$[Mo(NNH-CO-C_6H_5) (S_2CN(C_2H_2)a)a]$	3053.7	706.0	1618.5	1574.1
$(M_{2})^{(1)}(M_{2})^{(2)}(M_$	3070.1	712.8	1621.4	1591.5
$[Mo_2)(S_2 \in N(C_2 \Pi_5)_2)_3]$ $[Mo(NNH-CO-C_6H_5)-(S_C CN(CH_2)_2)_1]$	3056.6	696.4	1622.3	1571.2
$[Mo(NN-CO-C_6H_4-$	3070.1	709.9	1636.8	1593.4
$NO_2)(S_2CN(CH_3)_2)_3]$				

^a Out-of-plane bending.

¹ The MS shows a multiplet at m/z 690 which corresponds to the molecular ion, its isotopic distribution is consistent with only one molybdenum atom. Other multiplets appear at m/z 542 and 426, that correspond to $[Mo{S_2CN(C_2H_5)_2}_3]^+$ and $MoS{S_2CN(C_2H_5)_2}_2^+$, respectively.

Table 2				
Selected IR	bands for	or the	dialkyldithiocarbamato	ligands

Complex	v(C=N)	v(C–S)	v(-C-H)	v(-C-H)	v(CH)
$[Mo(NNH-CO-C_{\epsilon}H_{5})(S_{2}CN(C_{2}H_{5})_{2})_{3}]$	1506.6	1002.1	2980.4	2935.1	2873.3
$[Mo(NN-CO-C_6H_4-NO_2)(S_2CN(C_2H_5)_2)_3]$	1511.4	1009.9	2979.4	2935.1	2872.4
$[Mo(NNH-CO-C_6H_5)(S_2CN(CH_3)_2)_3]$	1539.4	999.2	2928.3	2858.9	
$[Mo(NN-CO-C_6H_4-NO_2)(S_2CN(CH_3)_2)_3]$	1524.9	1008.9	2931.2	2861.0	

shifted to lower frequency, the ligand is didentate. The IR spectra of 1, 2, 3, and 4 show two bands in the region 1640-1570 cm⁻¹ that may be assigned to either v(C=O), v(N=N), $\delta(N-H)$, or v(C=C) of the aromatic ring. This fact does not allow to establish the binding mode of the above mentioned ligands. In order to make a correct assignment, $[Mo(NNHCO-CH_3){S_2CN-}$ $(C_2H_5)_2$, and $[Mo(NN-Ph)\{S_2CN(C_2H_5)_2\}_3]$ were synthesized, the former lacking the aromatic group and the latter, the C=O group. The IR spectrum of the former also has the above mentioned bands, therefore it can be concluded that they do not originate from the v(C=C)of the aromatic ring of the *p*-nitrobenzoyldiazenido or benzoylhydrazido ligand. The IR spectrum of the latter does not have the band around 1620 cm^{-1} that is present in the *p*-nitrobenzoyldiazenido- and benzoylhydrazido complexes, and therefore it should correspond to v(C=O). On the other hand, the band around 1580 cm⁻¹ can still be assigned to δ (N–H) or ν (N=N). Compounds 2 and 4 do not have H bound to N, as is concluded from the ¹H NMR spectra but the IR spectra still show this band that can then be assigned to v(N=N). With the assignment of these bands we can conclude that the *p*-nitrobenzoyldiazenido and benzoylhydrazido ligands are acting as monodentate in all the complexes prepared. The band corresponding to v(N=N) is found at higher energy in the *p*-nitrobenzoyldiazenido(1-) complexes (around 1592 cm^{-1}) than in the benzoylhydrazido(2-)complexes (around 1572 cm^{-1}). This can be interpreted in terms of the decreasing N=N bond order when the ligand also has an N-H bond, since part of the electron density that is involved in the N=N bond is shifted to N-H.

3.4. NMR spectroscopy

3.4.1. ¹H NMR

The ¹H NMR spectra of **1** and **2** show the signals of the hydrogens from the diethyldithiocarbamates as complex multiplets at $\delta = 1.15-1.35$ and at $\delta = 3.62-$ 3.93, which are the result of overlapping of some triplets and quadruplets, respectively; this fact suggests that these coligands are not equivalent in solution. In **3** and **4** the hydrogens of the methyl groups from the dimethyldithiocarbamates give rise to four peaks in the range $\delta = 3.26-3.40$. In **1** and **3** the hydrogens of the benzyl ring of the benzoylhydrazido(2-) appear as two triplets and one doublet in the region $\delta = 7.27-8.12$, as expected [14]. In **2** and **4**, the hydrogens of the aromatic ring from the *p*-nitrobenzoyldiazenido display a multiplet at $\delta = 8.05-8.25$.

¹H NMR allows to determine whether the ligand is hydrazido or diazenido, since the number of hydrogens bound to the nitrogens determine the kind of ligand. The spectra of 1 and 3 show a broad signal at $\delta =$ 1.60-1.85 that disappears when D_2O is used. This behavior suggests that the band corresponds to the H bound to the non-coordinated N, then in these compounds the ligand is bound as benzoyl-hydrazido(2-); a similar signal was reported for [MoO(NNHPh)- $\{S_2CN(C_2H_5)_2\}_2$ [14]. When the hydrogen is bound to the coordinated nitrogen the signal is seen at higher chemical shift due to weaker binding, as found for [Mo(NHNPh₂)(NNPh₂)(acac)Cl₂] and [Mo(NHN-MePh)(NNMePh)(acac)Cl₂], where the signals appear by $\delta = 12$ [13]. Compounds **2** and **4** do not show signals assignable to hydrogen bound to nitrogen, and furthermore there are not changes in the spectra with D_2O_1 , then the ligand is bound as a p-nitrobenzoyldiazenido(1-).

Compound 2 shows a quintuplet at $\delta = 1.80-1.90$ that corresponds to one of the signals of THF, from the hydrogens bound to the carbons distant from oxygen. This quintuplet is not observed when the compound has not been recrystallized. The hydrogens bound to the carbons next to oxygen show a signal at $\delta = 3.70-3.80$ that overlaps with the signals from the coligands.

The integration ratios for compounds 1, 2, 3, and 4 are in agreement with the presence of three dialkyldithiocarbamato coligands and one *p*-nitrobenzoyldiazenido or benzoylhydrazido ligand.

3.4.2. ¹³C NMR

The ¹³C NMR spectra of **1** and **3** show four signals in the region $\delta = 127-135$ that correspond to the aromatic carbons from the benzoylhydrazido. In compounds **2** and **4**, four similar signals from the *p*-nitrobenzoyldiazenido are shown at 122–150. All four compounds show a signal at $\delta = 180$ that corresponds to C from the carbonyl group. The diethyldithiocarbamato coligands from 1 and 2 give signals around $\delta = 12$ and 42-45from the ethyl groups, whereas the methyl groups from 3 and 4 give signals at $\delta = 37-41$. All four compounds show two signals around $\delta = 200$ and 206 that correspond to the carbons bound to sulfur in the dialkyldithiocarbamates; of these, the former signal is approximately twice as intense as the latter, suggesting that only two of the coligands are equivalent and located on the same plane, which is consistent with a nearly decaedric geometry obtained for a seven coordination number.

3.5. Mass spectrometry

Compound 2 shows a Mo-isotopic multiplet with the most intense peak at m/z 721 which can be assigned to the protonated molecular ion, [Mo(NNHCO-C₆H₄-NO₂){S₂CN(C₂H₅)₂}₃]⁺. At m/z 542 another similar multiplet is found, that corresponds to the loss of the protonated ligand -NNHCO-C₆H₄-NO₂. The additional proton is not found in the ¹H NMR spectrum of the complex, therefore it is gained in the ionization process; these proton additions are common when the FAB-Nibeol ionization technique is used [19].

The mass spectrum of **5** shows a multiplet with the most intense peak at m/z 690, that can be assigned to the $[Mo\{S_2CN(C_2H_5)_2\}_4]^+$ ion, its isotopic distribution corresponds to a complex with one molybdenum atom; there are also multiplets at m/z 574, assigned to $[Mo-S\{S_2CN(C_2H_5)_2\}_3]^+$; m/z 542, assigned to $[Mo\{S_2CN-(C_2H_5)_2\}_3]^+$; m/z 426, assigned to $[Mo\{S_2CN-(C_2H_5)_2\}_2]^+$; and m/z 394, that corresponds to $[Mo\{S_2CN(C_2H_5)_2\}_2]^+$.

3.6. X-ray structure of $[Mo(NNCO-C_6H_4-NO_2){S_2CN(C_2H_5)_2}_3] \cdot (0.5)THF$ (2)

The X-ray structure of this compound is shown in Fig. 2. Crystal data are listed in Table 3 and the selected bond lengths and angles, in Table 4. The complete atomic coordinates, bond lengths and angles have been deposited as Supporting Information. The Mo atom is heptacoordinated, the donor atoms are arranged in a distorted pentagonal bipyramid. The atoms N5 and S1 occupy the axial positions (N5–Mo1–S1 166.1(2)°), while the atoms S2, S3, S4, S5, and S6 are located in the equatorial plane. S2 connected via C1 to the axial atom S1 deviates strongly



Fig. 2. Molecular structure of $[Mo(NN-CO-C_6H_4-NO_2)(S_2CN(C_2H_5)_2)_3]$ (2).

Table 4									
Salaatad	hand	longths	(Λ)	and	anglas	(°)	for	IM _o (NIN CO	

Crystal data for $[Mo(NN-CO-C_6H_4-NO_2)(S_2CN(C_2H_5)_2)_3]$ (2)

754.9

 $P2_{1}/a$

 $0.05 \times 0.25 \times 0.50$

monoclinic

10.546(5)

27.084(14)

12.251(6)

110.78(4)

3437(3)

90

90

4

1.46

7.8

23

1560

4786

4786

372

0.051

0.124

 $0 \le l \le 13$

 $[I > 2\sigma(I)]$ 3247

+0.6; -0.6

 $-11 \le h \le 11, \ 0 \le k \le 29,$

C22H34MoN6O3S6.0.5C4H8O

Table 3

Empirical formula

Crystal size (mm)

Unit cell dimensions

Formula weight

Crystal system

Space group

a (Å)

b (Å)

c (Å)

α (°)

 β (°)

γ (°)

 μ (cm⁻¹)

hkl range

Parameters

 $(e Å^{-3})$

F(000)

 $\theta_{\rm max}$

 $D_{\rm calc}~({\rm g~cm^{-3}})$

Reflections collected

Reflections observed

 R_1 (for observed data only)

Largest difference peak and hole

Reflections unique

 wR_2 (for all data)

 $V(Å^3)$

Ζ

Selected	bond	lengths	(A)	and	angles	(°)	for	[Mo(NN-CO-
C ₆ H ₄ –NO	D_2)(S_2C	$N(C_2H_5)$	2)3] (2	2)				

Mo(1)–N(5)	1.756(5)
Mo(1)–S(2)	2.490(2)
Mo(1)-S(5)	2.516(2)
Mo(1)–S(3)	2.522(2)
Mo(1)–S(6)	2.527(2)
Mo(1)-S(4)	2.531(2)
Mo(1)-S(1)	2.576(2)
C(16)-C(22)	1.513(9)
C(22)–O(1)	1.208(8)
C(22)–N(4)	1.382(9)
N(4)-N(5)	1.278(7)
N(5)-Mo(1)-S(2)	96.26(18)
N(5)-Mo(1)-S(5)	101.27(18)
N(5)-Mo(1)-S(3)	98.86(18)
N(5)-Mo(1)-S(6)	90.51(17)
N(5)-Mo(1)-S(4)	91.00(17)
N(5)-Mo(1)-S(1)	166.11(17)
S(2)-Mo(1)-S(1)	69.86(6)
S(5)-Mo(1)-S(1)	90.11(7)
S(3)-Mo(1)-S(1)	2.10(6)
S(6)-Mo(1)-S(1)	86.33(7)
S(4)-Mo(1)-S(1)	85.22(7)
O(1)-C(22)-N(4)	125.1(7)
O(1)-C(22)-C(16)	121.6(7)
N(4)-C(22)-C(16)	113.3(6)
N(5)-N(4)-C(22)	116.0(6)
N(4)-N(5)-Mo(1)	174.9(5)

from the plane through Mo1, S3, S4, S5 and S6. The MoS₂CNC₂ fragment from the diethyldithiocarbamato coligands is nearly planar as expected, and the bond distances lie in the expected ranges [9,20]. The Mo–N5–N4 group is nearly linear (175.4(9)°) indicating extensive electronic delocalization i.e., the Mo-N and N-N have double bond character or, in terms of the valence bond model, the N bound to Mo has sp hybridization. The Mo-N and N-N bond lengths (1.756(5) and 1.278(7) Å, respectively), are consistent with this character. Unfortunately, from X-ray studies it is not possible to establish whether the binding occurs as diazenido(1-) or hydrazido(2-), since comparison of $\frac{1}{2}$ bond lengths and angles (Mo-N-N-R_{1 or 2} fragment) for this ligands in similar compounds (Table 5) indicates that these values are within the same range. However, the double character of the Mo=N and N=N bonds is certain. There is a noticeable difference between these values and those observed for the hydrazido(1-) complexes, Mo-NH-NR₂, where the Mo-N and N-N bonds are single in character as indicated by the longer distances (1.95 and 1.38 Å, respectively), and smaller Mo-N-N angles (between 120 and 140°).

4. Conclusions

In the compounds prepared in this work, we found that bis(dialkyldithiocarbamato)-dioxocomplexes react with p-nitrobenzohydrazide and benzohydrazide to yield always seven-coordinate complexes, in which one oxo ligand is substituted by a hydrazide independently of the molar ratios of the hydrazide used, and the other oxoligand is substituted by an additional dialkyldithiocarbamato, even when this coligand is not added in the condensation reaction.

The aroyl hydrazines used in this work act as monodentate ligands, differently from the behavior reported for rhenium with phosphines as coligands, where the aroyl hydrazine preferentially coordinates in a didentate fashion.

Benzohydrazide and *p*-nitrobenzohydrazide have different behavior, the former gives ligands of hydrazido(2-) type while the latter, ligands of diazenido(1-) type. A plausible explanation for this difference is that when the $-NO_2$ group is present, electron density is withdrawn from the nitrogen atom and therefore the N–H bond is unstable. Molybdenum is reduced in this reactions, but the oxidation state of the metal is different in each ligand, thus Mo(V) complexes are obtained starting from Mo(VI) and benzohydrazide, while Mo(V) complexes are formed from *p*-nitrobenzohydrazide.

The study of IR spectra of the diazenido(1-) and hydrazido(2-) complexes, supported by the results of X ray diffraction and ¹H and ¹³C NMR allows to make a

Table 5

Complex	Mo–N	N–N	N–C	Mo-N-N	N–N–C	Reference
Diazenido (1-)						
$[Mo(NCO_2Et)(dtc)_3]$	1.732(5)	1.274(7)	1.382(10)	178.9(5)	117.0(6)	[21]
$[Mo(NNC_6H_4-3-NO_2)(S_2CNMe_2)_3]$	1.770(6)	1.262(9)	1.410(10)	170.6(6)	117.9(7)	[22]
[Mo(NNPh)(dmdtc) ₃],CH ₂ Cl ₂	1.781(4)	1.233(6)	1.417(7)	171.5(4)	120.5(5)	[23]
$[Mo{NNC_6H_4(m-NO_2)}(dmdtc)_3]_2,$	1.765(9),	1.268(13),	1.421(15),	170.0(9),	118.0(1.0),	[23]
1/2CH ₂ Cl ₂ , 1/2H ₂ O	1.776(9)	1.256(13)	1.400(14)	171.2(8)	117.8(1.0)	
$[Mo(NNC_6H_4Me-p)_2(acac)_2]$	1.80(3), 1.75(3)	1.27(3), 1.31(3)	1.37(4), 1.45(4)	176.0(28),	118.0(32),	[10]
				177.8(25)	120.5(28)	
[Mo(NNC ₆ H4OMe) ₂ (acac) ₂]	1.80(2), 1.75(2)	1.24(2), 1.23(2)	1.45(2), 1.44(2)	176.8(14),	120.3(14),	[10]
				174.9(13)	118.8(15)	
[Mo(PPh ₃)(N ^a NCOPh) ^b (N ^a NCO ^a Ph)(C ₁₀ H ₁₁ N ₂ O)]	1.785(8) ^b	1.29(1) ^b	1.40(1) ^b	171.0(6) ^b	111.9(8) ^b	[24]
Hidrazido (2-)						
[Mo(NNMePh)(NHNMePh)- (S ₂ CNMe ₂) ₂] ⁺	1.752(10)	1.285(14)		169.6(7)		[25]
$[Mo(NnMe_2)O(S_2CNMe_2)_2]$	1.799(8)	1.288(10)	1.485(13), 1.529(12)	168.0(7)	121.9(8), 117.3(9)	[26]
[Mo(NNPh ₂) ₂ (S ₂ CNMe ₂) ₂]	1.74(1)	1.31(1)	1.43(1), 1.45(1)	169.9(8)	118.8(5), 118.7(7)	[27]
$[Mo(NNEtPh)(S_2CN(CH_2)_5)_3]^+$	1.715(16)	1.37(2)		170(2)	118. 116	[28]
[MoO(NNMePh)(acac) ₂]	1.789(3)	1.281(4)	1.468(4),	175.6(2)	118.3(3),	[29]
. , , , , , , , , , , , , , , , , , , ,	. ,		1.419(4)		119.5(5)	
$[{MoO(NNMePh)(acac)(\mu-OPr-n)}_2]$	1.780(4)	1.292(6)	1.466(8),	165.5(4)	118.7(5),	[29]
			1.423(6)		120.2(5)	
[MoI(NNHC ₈ H ₁₇)(dppe) ₂] ⁺	1.801(11)	1.259(14)	1.505(17)	174(1)	120(1)	[30]
Hidrazido (1-) [°]						
[Mo(NHNPh ₂) ^c (NNPh ₂) ^d (acac)-	1.948(5) °	1.359(6) °	1.412(7),	140.5(4) °	119.4(5),	[11]
Cl ₂]	. ,		1.432(7) °		118.7(5) °	
	1.752(4) ^d	1.313(6) ^d	$1.433(7)^{d}$	171.9(4) ^d	118.1(4),	
	. ,				$118.4(4)^{d}$	
[Mo(NHNMePh) ^e (NNMePh) ^f (acac)-	1.948(2) ^e	1.339(3) °	1.443(4),	142.9(2) ^e	117.9(3),	[11]
Cl ₂]	× /	~ /	1.416(4) °	~ /	118.7(3) °	
	1.750(2) ^f	1.301(3) ^f	1.460(4),	173.8(2) ^f	116.9(2),	
			1.419(4) ^f		$120.3(2)^{f}$	

^a Coordinated atoms.

^b Values correspond to this part of molecule.

^c Values correspond to this part of molecule.

^d Values correspond to this part of molecule.

^e Values correspond to this part of molecule.

^f Values correspond to this part of molecule.

conclusive assignment of v(C=O) and v(N=N) vibrations, which in turn allows to establish the type of binding of the hydrazines as mono o didentate.

A singular behavior is observed for the dialkyldithiocarbamato coligands, since the number of these in the complexes successively increases in each step of the syntheses.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 137508. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk).

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