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Chromium(II) and Molybdenum(II) *N*,*N*-Diethylcarbamato Complexes from Metal Halides/CO_2/$NHEt_2$: Crystal and Molecular Structure of the Quadruply Metal–Metal-Bonded $Mo_2(O_2CNEt_2)_4$

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The reaction of $NHEt_2$ with CO_2 and chlorinated chromium(II) substrates yielded $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$ identical with the product obtained by a different route. The dichloride β-$MoCl_2$ reacts with the $NHEt_2/CO_2$ system to give $Mo_2(O_2CNEt_2)_4$ in good yields. Crystal data: $M_r = 658.4$; triclinic; space group $P1$; $a = 9.217(3)$, $b = 9.613(3)$, $c = 8.852(3)$ Å; $\alpha = 95.46(3)$, $\beta = 104.66(3)$, $\gamma = 63.12(3)°$; $V = 676.6$ Å^3; $Z = 1$; $D_c = 1.610$ g cm^{-3}. Each molybdenum atom in a square pyramidal geometry is surrounded by four carbamato oxygens, the Mo–Mo distance of the quadruply bonded system being 2.067(2) Å.

Introduction

The *N*,*N*-dialkylcarbamato complexes of chromium(II) and molybdenum(II) $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$[1] and $Mo_2(O_2CNEt_2)_4$,[2] respectively, which were obtained earlier, were synthesized by carbonation of the corresponding chromium(IV) and molybdenum(III) diethylamido complexes. The chromium(III) complex $Cr_2(O_2CNEt_2)_4(NEt_2)_2$ was also a product of the reaction between $Cr(NEt_2)_4$ and CO_2, its amount relative to the chromium(II) complex depending essentially on the initial CO_2 partial pressure. The reduction from chromium(IV) to chromium(II) was suggested to involve β-hydrogen elimination from coordinated NEt_2 groups. In view of these results and of our earlier experience[3] on the synthesis of *N*,*N*-dialkylcarbamato complexes from metal halides, secondary amines, and CO_2, we reckoned that the preparation of the chromium(II) and molybdenum(II) complexes could be achieved by using $CrCl_2$[4] or $CrCl_2\cdot n$THF[5] or β-$MoCl_2$[6] as starting materials.

In this paper we report the preparation of both complexes and the crystal and molecular structure of the molybdenum(II) species; moreover, X-ray powder diffraction data have shown the compound obtained by the chromium(II) chloride/Et_2NH/CO_2 route to be identical with $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$ reported earlier.[1] The molybdenum(II) species contains four diethylcarbamato bridges, a feature already encountered in the corresponding copper(II) system,[3g] and the molybdenum–molybdenum distance is 2.067(2) Å, among the shortest found in molybdenum(II) compounds with a quadruple metal–metal bond.[7]

Experimental Section

Unless otherwise stated, all the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents and organic reagents were purified by conventional methods. Commercial HI (Matheson) was used without further purification. $CrCl_2\cdot n$THF[8] and $Cr_2(O_2CMe)_4$[9] were prepared by a slightly modified literature method, while β-$MoCl_2$[6] and $CrCl_2$[4] were prepared according to the literature. The IR spectra were measured with a Perkin–Elmer Model 283 instrument equipped with a grating. The UV–vis spectra were measured with a Perkin-Elmer Hitachi 200 spectrophotometer. The thermogravimetric analyses were carried out with a DuPont 2000 thermal analyzer. The mass spectra were measured with a MS-5970 instrument. The magnetic measurements were carried out using the Faraday method. Elemental analyses (C, H, N) were performed at the Istituto di Chimica Farmaceutica, Università di Pisa, and chromium was titrated with EDTA solution or calcined to Cr_2O_3.

Preparation of $CrCl_2\cdot n$THF. The tetrahydrofuran adduct of chromium(II) chloride was prepared by treating chromium(II) acetate with acetyl chloride in tetrahydrofuran. Chromium(II) acetate (15.88 g, 93.36 mmol) suspended in THF (200 mL) was reacted at room temperature (about 25 °C) with CH_3COCl (20 mL, 22.1 g, 281 mmol). After the mixture was stirred for 10 h, a suspension of the pale-blue product in a nearly colorless medium was obtained. The solid was collected by filtration and dried under reduced pressure (19.25 g, 69% yield based on the chromium content). The product is extremely sensitive to oxygen and moisture. Anal. Calcd for $C_{10}H_{20}Cl_2CrO_{2.5}$ ($CrCl_2\cdot 2.5C_4H_8O$): Cr, 17.1. Found: Cr, 17.5. IR spectrum (polychlorotrifluoroethylene and Nujol mulls): 2980 s, 2920 sh, 2910 s, 2880 m, 1610 w, 1480 w, 1460 m, 1445 m, 1380 m-w, 1340 m, 1045 sh, 1020 s, 920 m-w, 865 s, and 720 m-w cm^{-1}.

When the reaction between chromium(II) acetate and CH_3COCl was carried out in acetic acid, the adduct $CrCl_2\cdot 1.5CH_3COOH$ was obtained.[8]

Preparation of $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$, 1. A solution of $NHEt_2$ (30 mL, 21.6 g, 295 mmol) was saturated with CO_2, and $CrCl_2\cdot 2.5$THF[10] (12.42 g, 40.97 mmol) was then added under CO_2. The mixture was stirred at room temperature for 6 h. The suspension of a colorless solid in a red-wine supernatant liquid was filtered, and the filtrate was evaporated to dryness. The residue was dissolved with heptane (25 mL) and stored in a freezer (−30 °C) under argon for 24 h. The wine red

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(10) Good results were also obtained starting from anhydrous $CrCl_2$.[4] We are grateful to Dr. C. Bellitto, Istituto di Teoria e Struttura Elettronica dei Composti di Coordinazione, CNR, Area della ricerca di Roma, I-00016 Monterotondo, Roma, Italy, for supplying a sample of the chloride.

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chromium(II) derivative was filtered off, dried under reduced pressure, and sealed in vials under argon (11.06 g, 75% yield). A second crop of the product was obtained from the filtrate, after storage at about −30 °C for a day (0.80 g, 81% total yield). The compound is sensitive to air and soluble in aromatic hydrocarbons and in oxygenated solvents. Anal. Calcd for $C_{28}H_{62}Cr_2N_6O_8$: Cr, 14.6; C, 47.0; H, 8.7; N, 11.8; CO_2, 24.6. Found: Cr, 14.8; C, 45.4; H, 9.0; N, 11.4; CO_2, 23.5. IR spectrum (KBr windows, C_2Cl_4 solution, 4000–1300 cm^{-1}; Nujol mull, 1300–600 cm^{-1}; polyethylene windows and heptane solution, 600–200 cm^{-1}): 2970 s, 2930 m-s, 2870 m-w, 1578 s, 1560 sh, 1510 sh, 1498 s, 1460 m, 1433 s, 1378 m, 1318 s, 1215 m, 1155 m-w, 1090 m (br), 970 m, 935 w, 840 w, 810 sh, 790 s, 720 m-s, 638 m-s, 480 m (br), 385 w (br), and 315 m (br) cm^{-1}. UV–vis spectrum (700–300 nm), 10^{-2} M heptane solution: λ_{max} (nm), ϵ (M^{-1} cm^{-1}) in parentheses: 480 (~60), 324 (~250); after oxidation by air, 585 (~70), 395 (~95). In a thermogravimetric experiment (heating rate 20 deg min^{-1}; maximum temperature, 334 °C) the sample lost 66.4% of its original weight, corresponding to the formation of $Cr_2(CO_3)_2O$. The lattice constants of a small (about 0.1 × 0.1 × 0.2 mm^3) crystal were determined on an ENRAF-Nonius CAD 4 diffractometer by least-squares refinement of 25 reflections. All reflections could be indexed assuming a triclinic cell, and the lattice constants were, within experimental error, identical with those reported earlier.[1]

Synthesis of $Mo_2(O_2CNEt_2)_4$, 2. A suspension of β-$MoCl_2$[6] (3.175 g, 19.03 mmol) in 200 mL of toluene was treated with 10 mL of $NHEt_2$ (7.1 g, 97.07 mmol) and saturated with CO_2. The flask, connected with a 4-L reservoir filled with CO_2, was heated at 70 °C for 3 days under stirring. The slightly brown solid (constituted by NH_2Et_2Cl and some unreacted metal chloride) was removed by filtration, and the brown yellow solution was evaporated to dryness. To the residue was added 150 mL of boiling heptane; by filtration of the hot solution and cooling to room temperature, 1.349 g of the product was obtained as a yellow microcrystalline solid. Cooling to about −30 °C of the mother liquor gave another crop (0.770 g) of the carbamato complex, the total yield being 34%. Anal. Calcd for $C_{20}H_{40}Mo_2N_4O_8$: C, 36.5; H, 6.1; N, 8.8; CO_2, 26.7. Found: C, 36.1; H, 6.1; N, 8.3; CO_2, 26.4. The compound is sensitive to air, but large crystals can be handled in air for a few seconds without appreciable decomposition. IR spectrum (C_2Cl_4 solution, 4000–1300 cm^{-1}; Nujol mull, 1300–400 cm^{-1}): 2970 s, 2930 m-s, 2870 m-w, 1510 s, 1460 w, 1435 m-s, 1380 m, 1315 s, 1210 w, 1130 m, 1090 w, 970 w, 940 w, 850 w, 810 w, 780 m, 770 m, 625 m, 450 w cm^{-1}. UV–vis spectrum (700–300 nm), 8×10^{-3} M THF solution; λ_{max} (nm), ϵ (M^{-1} cm^{-1}) in parenthesis: 470 (173). Magnetic susceptibility: $\chi^{corr}(T = 298\ K) = -72 \times 10^{-6}$ emu; diamagnetic correction = -163×10^{-6} emu.

X-ray Data Collection and Refinement for $Mo_2(O_2CNEt_2)_4$. Recrystallization from heptane gave yellow needles used for the X-ray diffraction experiment. A crystal of dimensions (mm) 0.05 × 0.05 × 0.8 was sealed under argon in a glass capillary. An Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation was employed (T = 20 °C, λ = 0.7107 Å). By a least-squares refinement based on 25 reflections, the following crystal data were obtained: a = 9.217(3), b = 9.613(3), c = 8.852(3) Å; α = 95.46(3), β = 104.66(3), γ = 63.12(3)°; V = 676.6 Å^3; Z = 1, D_c = 1.610 g cm^{-3}. The space group was $P\bar{1}$, No. 2, in ref 11. In the θ range 3–24°, 2258 reflections were recorded on half the reflection sphere ($\pm h, \pm k, +l$). Averaging the symmetry-equivalent data left 1724 independent reflections with $I > 3\sigma(I)$. From the $2x$, $2y$, $2z$ inversion peak of a Patterson synthesis,[12] the metal atom position was calculated. A difference Fourier synthesis showed all the non-hydrogen atoms. The atoms were refined isotropically; an empirical absorption correction[13] was applied on the original data set, and merging of the equivalent reflections was repeated. At this stage, the agreement factor was 0.045. Anisotropic thermal parameters were introduced for all the atoms, and a subsequent Fourier synthesis showed 17 out of the 20 hydrogen atoms. These and the remaining hydrogen atoms were not refined but included in structure factors calculation. In the final refinement cycle, a correction for secondary extinction was applied on F_c,[14] giving R = 0.037 and R_w = 0.042 ($w = 1/\sigma(I)^2$), using 1664 reflections with $I > 4\sigma(I)$ for 154 parameters. Atomic coordinates are in Table I.

Table I. Positional Parameters for $Mo(O_2CNEt_2)_4$[a]

atom	x	y	z	B (Å^2)
Mo1	0.47925(6)	0.08770(6)	0.08079(6)	2.47(1)
O1	0.5684(5)	0.7449(4)	0.0865(5)	3.2(1)
O2	0.2195(4)	0.1557(4)	0.0248(5)	3.1(1)
O3	0.2640(4)	−0.0355(4)	−0.1502(5)	2.93(9)
O4	0.5214(5)	0.9348(4)	0.2616(4)	3.11(9)
N1	0.6204(6)	0.6852(5)	0.3413(6)	3.7(1)
N2	0.0022(6)	0.8708(6)	0.1295(6)	3.5(1)
C1	0.5684(7)	0.7917(6)	0.2261(7)	3.1(1)
C2	0.1646(7)	0.0820(6)	−0.0843(7)	3.1(1)
C11	0.6346(8)	0.7348(7)	0.5037(7)	3.8(2)
C12	0.7080(8)	0.5160(8)	0.3093(8)	4.4(2)
C13	0.8005(9)	0.731(1)	0.578(1)	5.8(2)
C14	0.5910(9)	0.4456(9)	0.257(1)	6.2(2)
C21	0.1138(8)	0.7320(8)	0.0600(8)	4.3(2)
C22	0.0735(7)	0.9489(7)	0.2524(8)	4.0(2)
C23	0.1382(9)	0.5806(8)	0.128(1)	5.4(2)
C24	0.161(1)	0.8600(9)	0.4056(9)	5.3(2)

[a] Estimated standard deviations in parentheses refer to the least significant figure. Hydrogen atoms were not refined but were included in structure factors calculations. Anisotropically refined atoms are given in the form of isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

Reactions of 1. (a) With Acetylacetone. A 0.19 M solution of acacH in heptane (19.2 mL, 3.65 mmol) was added dropwise to **1** (0.774 g, 1.08 mmol) partially dissolved in 100 mL of heptane (molar ratio acacH/Cr = 1.7). After it was stirred for 1 h, the resulting suspension was filtered and the yellow solid thus obtained was dried under reduced pressure (0.309 g, 67.7% yield based on the acacH employed) and gave a correct elemental analysis for $Cr(acac)_2$.[15] IR spectrum, C_2Cl_4 solution: 1575 vs, 1550 s, 1520 vs, 1390 s (br), 1355 s, 1280 sh, 1270 m, 1260 m, 1220 w, and 1190 w cm^{-1}.

In another experiment, the reaction was carried out by gradual addition of acetylacetone to **1** (0.395 g, 0.55 mmol). In a 250-mL flask, **1** was dissolved in 50 mL of heptane and a solution of acacH in heptane was added portionwise. After the addition of 2 equiv of acetylacetone, the yellow precipitate of $Cr(acac)_2$ was observed; the addition of the third equivalent caused the formation of the violet $Cr(acac)_3$,[16] with the expected mass fragmentation: no M + 1 or M + 2 masses were observed.

(b) With HI. To a solution of **1** (2.06 g, 2.88 mmol) in heptane (150 mL), an excess of dry HI was added at atmospheric pressure. An immediate reaction occurred, as shown by a sequence of color changes from blue to violet to black through light green. After the mixture was stirred for 1 h, the black solid was filtered off and dried in vacuo (5.03 g, 96% yield calculated for the 1:1 mixture $(NH_2Et_2)_2CrI_4 + NH_2Et_2I$). Anal. Calcd: Cr, 5.7. Found: Cr, 5.4. A portion of the solid (2.03 g) was washed with CH_2Cl_2 to eliminate NH_2Et_2I, and the solid left behind was filtered off and dried under reduced pressure (42.6% yield based on the starting chromium complex). Anal. Calcd for $(NH_2Et_2)_2CrI_4$, $C_8H_{24}CrI_4N_2$: Cr, 7.3. Found: Cr, 7.7. The product is very sensitive to oxygen and moisture. IR spectrum (polychlorotrifluoroethylene and Nujol mulls): 3100 s (br), 3000 m-s, 2980 w, 2960 w, 2940 w, 2880 w, 2820 w, 2780 w, 2420 w, 2320 w, 1560 sh, 1555 m, 1540 sh, 1460 s, 1450 m, 1413 m, 1403 w, 1395 m, 1350 w, 1260 w, 1155 w, 1030 w, 870 w, 800 w (br), 757 m-w, 748 m-w, and 720 w cm^{-1}. Magnetic susceptibility: Curie–Weiss type behavior in the temperature range 295–100 K, θ = −17 K, C = 2.6, μ_{295} = 4.6 μ_B.

(c) With I_2. To a solution of **1** (1.20 g, 1.68 mmol) in heptane (50 mL) a solution of I_2 (0.426 g, 1.68 mmol) in heptane (50 mL) was added dropwise at room temperature. The green solid was collected by filtration and dried in vacuo (0.64 g, 61% yield of a product analyzing as $CrI(O_2CNEt_2)_2(NHEt_2)$). Anal. Calcd for $C_{14}H_{31}CrIN_3O_4$: C, 34.7; H, 6.4; N, 8.7; Cr, 10.7. Found: C, 35.2; H, 6.2; N, 8.6; Cr, 11.5 IR spectrum (PCTFE and Nujol mull): 2970 m-s, 2930 m-s, 2870 m, 1600 sh, 1570 s (br), 1515 vs (br), 1430 vs, 1380 s, 1320 s (br), 1215 m, 1100 m, 1070 m, 970 m, 940 m-w, 840 m, 800 m-s, 790 sh, 780 sh, 770 sh, 730 m, 720 m, 670 sh, 645 m-s, 630 sh, 600 m-w, and 475 m (br) cm^{-1}.

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Results and Discussion

Synthesis of Complexes. The *N,N*-diethylcarbamato complex of chromium(II), $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$, was prepared by the reaction of $CrCl_2$,[17-19] either unsolvated[4] or as its tetrahydrofuran adduct $CrCl_2{\cdot}n$THF, with diethylamine and carbon dioxide at atmospheric pressure: the reaction is rather facile, as expected for a chromium(II) system of d^4 configuration,[20] and is believed to occur via the in situ formation of the diethylcarbamato anion, followed by exchange with the chloride ligand; see eqs 1 and 2.

$$4Et_2NH + 2CO_2 \rightarrow 2NH_2Et_2(O_2CNEt_2) \qquad (1)$$

$$Et_2NH + 2NH_2Et_2(O_2CNEt_2) + CrCl_2 \rightarrow 2NH_2Et_2Cl + {}^1/_2Cr_2(O_2CNEt_2)_4(NHEt_2)_2 \qquad (2)$$

$$\text{net:} \quad 5Et_2NH + 2CO_2 + CrCl_2 \rightarrow 2NH_2Et_2Cl + {}^1/_2Cr_2(O_2CNEt_2)_4(NHEt_2)_2 \qquad (3)$$

The *N,N*-diethylcarbamato complex obtained by the overall reaction 3 is well soluble in the reaction medium (toluene) and can be recovered from it, after elimination of NH_2Et_2Cl by filtration, on cooling at about −30 °C.

The preparation of $Mo_2(O_2CNEt_2)_4$ was similarly carried out starting from β-$MoCl_2$, according to eq 4; the product does not

$$4Et_2NH + 2CO_2 + MoCl_2 \rightarrow {}^1/_2Mo_2(O_2CNEt_2)_4 + 2NH_2Et_2Cl \qquad (4)$$

retain any coordinated amine. The *N,N*-diethylcarbamato complex of molybdenum(II) has been mentioned in the literature,[2] as the product resulting from the carbonation of the diethylamido complex of molybdenum(III), $Mo_2(NEt_2)_6$. The present reaction represents the first preparation of this compound by a straightforward method, not involving electron-transfer processes, and requiring the readily available $MoCl_2$ as starting material.

Crystal and Molecular Structure. As the crystal and molecular structure of the *N,N*-diethylcarbamato complex of chromium(II) was already known,[1] we confined ourselves to verify that the compound obtained by our synthetic method was the same as that reported earlier. It has already[1] been noted that the chromium(II) system produced a relatively long chromium–chromium bond of 2.384(2) Å, as compared with what was expected for a quadruply bonded system.[21,22] With the new results available[3g] on the isostructural copper(II) system $Cu_2(O_2CNEt_2)_4(NHEt_2)_2$, belonging to the same space group ($P\bar{1}$) and with similar cell constants, it is possible to confirm that, ceteris paribus, the electronic configuration of the metal has a specific influence on the intermetallic bond distance; although longer than expected, the chromium–chromium distance is a lot (about 0.3 Å) shorter than the Cu···Cu distance of 2.658(2) Å in the copper(II) system, where no fully formed intermetallic bond is required to explain the magnetic properties, a relatively small degree of antiferromagnetic coupling, $2J = -80.2(4)$ cm^{-1}, being observed. A similar situation applies to the acetato complexes of copper(II) and chromium(II),[23-29] where the difference in the M–M distance in isostructural complexes is between 0.21 and 0.35 Å.

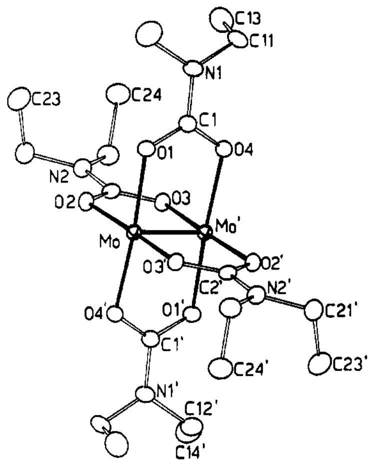

Figure 1. ORTEP drawing of $Mo_2(O_2CNEt_2)_4$ with the numbering scheme used.

Related to the discussion on the multiple chromium–chromium bond in compound **1** are the structural parameters of **2**, $Mo_2(O_2CNEt_2)_4$. A view of the molecular structure of this compound is shown in Figure 1, and bond distances and angles are in Table II. The structure consists of dimeric units resulting from the fusion of two molybdenum(II) pyramids along the Mo–Mo bond of 2.067(2) Å in an eclipsed conformation. The Mo_2O_8 unit has therefore virtual D_{4h} symmetry. The molybdenum–molybdenum distance in our case is the shortest among those crystallographically established for molybdenum(II) dimeric species by making reference for convenience to molybdenum(II) carboxylates only ($Mo_2(O_2CR)_4$: R = H,[30] 2.091(2); R = Me,[31] 2.093(1) Å). Most interesting is the fact that additional axial coordination of water in $Mo_2(O_2CH)_4(H_2O)_2$[32] does not appear to greatly modify the Mo–Mo distance (2.100(1) Å). Moreover, molybdenum(II) carboxylates of the type $Mo_2(O_2CR)_4$ have been found to experience an axial coordination from the neighbors leading to infinite chains.[33] However, once again this does not appear to alter greatly the molybdenum–molybdenum distance: for example the electron diffraction study[34a] of gaseous $Mo_2(O_2CCF_3)_4$ has shown that the molybdenum–molybdenum distance is 2.105(9) Å, i.e. only 0.01 Å higher than in the solid state.[34b] In our case, the intermolecular interactions are reduced

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(17) The preparation of $CrCl_2$ requires the action of acetyl chloride on chromium(II) acetate,[8] in a reaction which should be regarded as the result of an electrophilic attack by the acetyl reagent on the carboxylate oxygen. Several other examples of this type of reactivity are well established in the literature for both metal carboxylates[18] and metal *N,N*-dialkylcarbamates.[3i,19] However, the literature procedure,[8] carried out in acetic acid as medium, leads to chromium(II) acetate solvated with acetic acid. In order to avoid possible complications arising from the presence of acetic acid in the system, the preparation of $CrCl_2$ was carried out in tetrahydrofuran as the medium.

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Table II. Relevant Bond Distances (Å) and Angles (deg) for $Mo_2(O_2CNEt_2)_4$[a]

Mo1–Mo1	2.067(2)	N1–C11	1.464(8)
Mo1–O1	2.113(4)	N1–C12	1.490(8)
Mo1–O2	2.110(4)	N2–C2	1.350(7)
Mo1–O3	2.118(4)	N2–C21	1.463(8)
Mo1–O4	2.120(4)	N2–C22	1.452(8)
O1–C1	1.275(7)	C11–C13	1.50(1)
O2–C2	1.280(7)	C12–C14	1.48(1)
O3–C2	1.290(7)	C21–C23	1.53(1)
O4–C1	1.275(7)	C22–C24	1.505(9)
N1–C1	1.352(7)		

Mo1–Mo1–O1	92.4(2)	C1–N1–C12	119.6(5)
Mo1–Mo1–O2	92.3(2)	C11–N1–C12	118.8(5)
Mo1–Mo1–O3	92.5(2)	C2–N2–C21	119.1(6)
Mo1–Mo1–O4	92.2(2)	C2–N2–C22	121.4(5)
O1–Mo1–O2	87.6(2)	C21–N2–C22	119.4(5)
O1–Mo1–O3	91.9(2)	O1–C1–O4	122.7(5)
O1–Mo1–O4	175.3(2)	O1–C1–N1	118.6(5)
O2–Mo1–O3	175.2(2)	O4–C1–N1	118.7(5)
O2–Mo1–O4	91.7(2)	O2–C2–O3	121.9(5)
O3–Mo1–O4	88.4(2)	O2–C2–N2	118.3(5)
Mo1–O1–C1	116.1(3)	O3–C2–N2	119.8(5)
Mo1–O2–C2	116.9(3)	N1–C11–C13	113.1(6)
Mo1–O3–C2	116.1(3)	N1–C12–C14	112.3(7)
Mo1–O4–C1	115.9(3)	N2–C21–C23	112.6(6)
C1–N1–C11	119.3(5)	N2–C22–C24	115.3(5)

[a] Numbers in parentheses are esd's in the least significant digit.

to a minimum, the shortest intermolecular distance being 4.08 and 4.09 Å between each molybdenum atom of a dimeric unit and the C11 and C14 atoms, respectively, of the nearest dimeric units. Therefore, the molybdenum centers in our system may be regarded as strictly pentacoordinate in a regular square pyramidal geometry. The metal–oxygen distance (2.115(4) Å, average) can be compared with the value of 2.018(7) Å found in the corresponding chromium complex. The difference in metallic radii between molybdenum and chromium has been reported to be 0.11 Å.[35a] The difference in the crystal radii between molybdenum(III) and chromium(III) is 0.08 Å.[35b] It is therefore reasonable to assume that the difference of the ionic radii between chromium(II) and molybdenum(II) would be around 0.1 Å, which corresponds to the values of the metal–oxygen distances reported above. The Mo–O distance in the carbamato complex compares well with the corresponding Mo–O distance observed in $Mo_2(O_2CMe)_4$.[31] Finally, the carbamato ligand in our molybdenum(II) complex is planar, the O_2CNC_2 atoms being displaced from the best plane by no more than 0.1 Å.

Table III. Relevant IR Bands (1600–1200 cm^{-1}) of Dimeric and Tetrameric *N*,*N*-Dialkylcarbamato Complexes Containing a Homogeneous Set of Bridging Ligands

compd (solvent)	IR bands, cm^{-1}	ref
$Cr_2(O_2CNEt_2)_4(NHEt_2)_2(C_2Cl_4)$	1578 s, 1498 s, 1460 m, 1433 s, 1378 m, 1318 s, 1215 m	this work[a]
$Cu_2(O_2CNEt_2)_4(NHEt_2)_2$(PCTFE[b])	1575 s, 1550 s, 1480 s, 1460 m, 1420 s, 1375 m, 1300 s	3g
$Mo_2(O_2CNEt_2)_4$(Nujol)	1510 s, 1460 w, 1435 m-s, 1380 m, 1315 s, 1210 w	this work
$Zn_4O(O_2CNEt_2)_6$(Nujol)	1570 vs, 1510 vs, 1460 s, 1430 s, 1380 s, 1320 s, 1220 s	34

[a] Reference 1 does not report bands above 1346 cm^{-1}. [b] Polychlorotrifluoroethylene.

Table IV. Low-Frequency Band in the Electronic Spectrum of Species Containing the M_2 Core

compd	solvent	λ_{max},[a] nm	ref
$Cr_2(O_2CNEt_2)_4(NHEt_2)_2$	THF	465 (56)	this work
$Mo_2(O_2CNEt_2)_4$	THF	470 (173)	this work
$Cr_2(O_2CMe)_4$	THF	463 (60)	this work
$Cr_2(O_2CMe)_4(H_2O)_2$	*b*	476	38b
$Mo_2(O_2CMe_2)_4$	EtOH	440 (60)	38a

[a] Molar extinction coefficient ϵ (M^{-1} cm^{-1}) in parentheses. [b] Single crystal.

Spectroscopic Properties. The chromium(II) derivative, isostructural with the corresponding copper(II) complex, has carbamato groups of only one type. This feature is not frequently encountered among *N*,*N*-dialkylcarbamato complexes and is common, in addition to the molybdenum complex which lacks the axial amine ligands, to $Zn_4O(O_2CNEt_2)_6$, which also has bridging bidentate carbamato groups exclusively.[36] It is therefore worth comparing the IR data for the four compounds, in the 1600–1200-cm^{-1} region, which usually contains the vibrations associated with the carbamato ligand; see Table III. The IR data of Table III suggest that the bridging bidentate coordination is characterized by bands below 1600 cm^{-1}. In this connection it is interesting to note that the terminal monodentate mode of coordination gives rise to a C–O stretching vibration at 1710–1720 cm^{-1} as observed in $Si(O_2CNR_2)_4$.[37] Intramolecular hydrogen bonding may lower ν_{CO} of monodentate dialkylcarbamato groups as observed in the case[38] of the palladium(II) complex *trans*-$Pd(O_2CNEt_2)_2(NHEt_2)_2$ containing hydrogen-bonded groups in a mutual cis position.

The electronic spectrum of $Cr_2(O_2CNEt_2)_4(NHEt_2)_2$, which had not been measured earlier,[1] shows bands at 480 and 324 nm in heptane as solvent.[39] Table IV reports the electronic absorption spectra of some dimeric *N*,*N*-dialkylcarbamato and acetato complexes. Either in solution or in the single crystal, the dimeric carbamato or acetato complexes, with or without an axial ligand, present a band[40] between 440 and 476 nm, recently assigned to a metal-localized spin-allowed δ–δ^* transition,[40c] i.e. a $^1A_{1g} \rightarrow {}^1A_{2u}$ or a $^1A_1 \rightarrow {}^1B_2$ transition in the D_{4h} (eclipsed) or D_{2d} (staggered) symmetry, respectively.

Reactivity of the Chromium(II) *N*,*N*-Diethylcarbamato Complex. The chromium(II) complex was reacted with acetylacetone in a molar ratio somewhat higher than 1:2 and found to form $Cr(acac)_2$, already reported in the literature, as prepared from chromium(II) acetate and acacH in aqueous solution:[15] the crystal and molecular structure has also appeared.[15c] Further reaction of the yellow bis(acetylacetonato) complex of chromium(II) with a third equivalent of acacH produces $Cr(acac)_3$. The stoichiometry can therefore be represented as shown in eqs 5 and 6,

$$\tfrac{1}{2}Cr_2(O_2CNEt_2)_4(NHEt_2)_2 + 2acacH \rightarrow Cr(acac)_2 + 3NHEt_2 + 2CO_2 \quad (5)$$

$$Cr(acac)_2 + acacH \rightarrow \tfrac{1}{2}H_2 + Cr(acac)_3 \quad (6)$$

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although we failed to detect H_2 in the reaction mixture. It is to be noted that the first stage of the reaction to form $Cr(acac)_2$ may be regarded as an electrophilic attack by acacH on the carbamato oxygen. Mild reaction conditions are used, and eq 5 can therefore be regarded as an alternative method of preparation of $Cr(acac)_2$.

The *N,N*-diethylcarbamato complex of chromium(II) also reacts promptly with dry HI in heptane giving a 1:1 mixture of $(NH_2Et_2)_2CrI_4$ and NH_2Et_2I, which could easily be separated by washing the precipitate with CH_2Cl_2. $(NH_2Et_2)_2CrI_4$ thus obtained, see eq 7, is a magnetically dilute high-spin complex,

$$Cr_2(O_2CNEt_2)_4(NHEt_2)_2 + 10HI \rightarrow 2(NH_2Et_2)_2CrI_4 + 2NH_2Et_2I + 4CO_2 \quad (7)$$

presumably constituted by mononuclear tetrahedrally coordinated $[CrI_4]^{2-}$ anions. Chromium(II) anionic halo complexes are known, namely $MCrX_3$,[41] M_2CrX_4,[42] and M_4CrX_6,[43] with M = univalent cation. In general these compounds contain hexacoordinated chromium in a distorted octahedral geometry. Salts containing the $[CrX_6]^{4-}$ anions are magnetically dilute systems, and compounds of formula $MCrX_3$ and M_2CrX_4 contain halide-bridged polynuclear anions with ferromagnetic or antiferromagnetic[41–43] behavior. Our compound therefore seems to be a unique example of a magnetically dilute M_2CrX_4 system, presumably due to the presence of the rather bulky diethylammonium cation.

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Supplementary Material Available: Tables of positional parameters, thermal parameters, and complete bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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