Synthesis and Co-ordination Chemistry of the Macrocycle 1,4,7-Triisopropyl-1,4,7-triazacyclononane†

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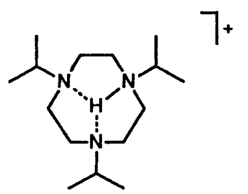
The bulky tridentate macrocycle 1,4,7-triisopropyl-1,4,7-triazacyclononane (L) has been prepared and its co-ordination chemistry investigated. Reaction of L with [M(CO)$_6$] in refluxing mesitylene affords air-stable [ML(CO)$_3$] (M = Cr **1**, Mo **2** or W **3**) in excellent yields. Oxidation of complexes **1** and **2** with SOCl$_2$ in CCl$_4$ yields [MLCl$_3$] (M = Cr **4** or Mo **5**) whereas [MLBr$_3$] (M = Cr **6** or Mo **7**) were obtained by using bromine as oxidant in CHCl$_3$. Exhaustive oxidative decarbonylation of **2** in semi-concentrated nitric acid affords colourless [MoLO$_3$]·3H$_2$O **8** which reacts with phenyl isocyanate in dry toluene yielding [MoLO$_3$]·(PhNH)$_2$CO **9**. In dry MeCN the ligand reacts with VCl$_3$ to give [VLCl$_3$] **10** which undergoes ligand substitution in water in the presence of NaSCN to give [VL(NCS)$_3$] **11**. When this reaction was carried out in the presence of oxygen [VOL(NCS)$_2$] **12** was obtained. The molecular structures of **2**, **8** and **9** have been established by single-crystal X-ray analysis.

The co-ordination chemistry of the tridentate, facially bound azamacrocycle 1,4,7-triazacyclononane and its *N*-methylated derivative 1,4,7-trimethyl-1,4,7-triazacyclononane has been extensively studied.[1,2] One of the most useful aspects of its chemistry is the enormous thermodynamic and kinetic stability of the (amine)metal fragment regardless of the oxidation state and d^n electronic configuration of the central metal ion. Thus in octahedral complexes these ligands serve as an effective blocking group for three co-ordination sites which allows a wide variety of chemical permutations at the other three sites including oligomerization reactions. We have now extended these studies by introducing a sterically more demanding innocent substituent at the nitrogen donor atoms. The methyl[3] and benzyl[4] derivatives have been synthesized previously. We here report the synthesis and some co-ordination chemistry of the new ligand 1,4,7-triisopropyl-1,4,7-triazacyclononane (L). We have found that complexes containing the LM fragment are in general readily soluble in polar and non-polar organic solvents and that the crystallization properties of complexes are in many cases excellent affording crystals suitable for single-crystal X-ray analysis. A further important feature of this ligand is that the three isopropyl substituents do not allow strong intermolecular bonding contacts (hydrogen bonding) which is a very useful property for the investigation of unperturbed intramolecular physical properties (magnetism) of a given molecule or ion in the solid state.

Results and Discussion

Syntheses and Spectroscopy.—The ligand 1,4,7-triisopropyl-1,4,7-triazacyclononane (L) is obtained by reaction of 1,4,7-triazacyclononane with isopropyl bromide (1 : 4) in toluene over solid KOH at 80–90 °C. After removal of KBr by filtration and evaporation of the solvent the resulting mixture of mono-, di- and tri-*N*-substituted derivatives is dissolved in methanol. Addition of NaClO$_4$ and water initiates the precipitation of [HL][ClO$_4$] as colourless crystals. Only the desired tri-*N*-substituted monohydroperchlorate precipitates. This procedure is therefore an efficient separation step. The free base is readily available from the hydroperchlorate by reaction in toluene with KOH, in 66% yield based on 1,4,7-triazacyclononane. The 80 MHz ^{1}H NMR spectrum in CDCl$_3$ exhibits the expected resonances at δ 0.9 [d, 18 H, CH(C*H*$_3$)$_2$], 2.5 [s, 12 H, N(CH$_2$)$_2$N] and 2.8 [m, 3 H, NC*H*(CH$_3$)$_2$].



In the infrared spectrum of [HL][ClO$_4$] a broad band at 2450 cm^{-1} is typical for a ν(N–H) stretching frequency where the NH proton is intramolecularly hydrogen bonded to two further amine nitrogen atoms. This structural motif has been established previously for 1,4,7-trimethyl-1,4,7-triazacyclononane hydroperchlorate by X-ray crystallography,[5,‡] It readily explains the large formation constant of the monoprotonated form of L (pK_a > 14). A consequence of this for the synthesis of transition-metal complexes is that care must be taken to avoid the presence of ionizable protons in the reaction mixture (water, alcohol). Once the LM fragment has formed the enormous kinetic stability of the co-ordinated ligand L prevents quite effectively ligand dissociation and concomitant formation of [HL]$^+$.

Reaction of the hexacarbonylmetal complexes [M(CO)$_6$] (M = Cr, Mo or W) with L in mesitylene at elevated temperature[6,7] affords yellow microcrystals of [ML(CO)$_3$] (M = Cr **1**, Mo **2** or W **3**). Compounds **1**–**3** are air-stable, useful starting materials for the synthesis of complexes containing the LM fragment. They have C_3 symmetry (see below) or C_{3v} local

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ We have determined the crystal structure of the salt [HL][FeCl$_4$] by X-ray crystallography: rhombic, space group *Pcab* (no. 61), a = 15.150(7), b = 17.413(7), c = 17.966(8) Å, U = 4739.6 Å^3, Z = 8, D_c = 1.27 g cm^{-3}. The monoprotonated nine-membered macrocyclic ring has the configuration shown schematically in the text. Details of this structure determination will be published elsewhere.

Table 1 Vibrational spectroscopic data (cm^{-1}) for carbonyl complexes

Complex	ν(CO)	Ref.
1	1886, 1750, 1720	This work
2	1892, 1741, 1720	This work
3	1881, 1740, 1720	This work
[Mo(dien)(CO)$_3$]	1887, 1734	11
[Mo([9]aneS$_3$)(CO)$_3$]	1915, 1783	8
[Mo([12]aneP$_3$)(CO)$_3$]	1945, 1844	9
[Mo(CO)$_6$]	2115, 1983	10

Ligand abbreviations: [9]aneS$_3$ = 1,4,7-trithiacyclononane; [12]-aneP$_3$ = 1,5,9-triphosphacyclododecane.

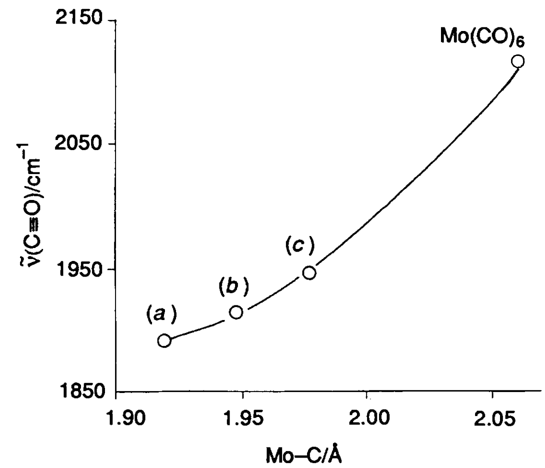

Fig. 1 Correlation of the ν(CO) stretching frequency and the Mo–CO bond distance in *fac*-[Mo(CO)$_3$] complexes with (*a*) 1,4,7-triisopropyl-1,4,7-triazacyclononane, (*b*) 1,4,7-trithiacyclononane and (*c*) 1,5,9-triphosphacyclododecane

symmetry if one considers only the nitrogen atoms and the carbonyl ligands. Therefore, in the infrared spectrum two ν(CO) stretching frequencies (A_1,E) are observed (Table 1). The degeneracy of the E mode is lifted in the solid state. In the Raman spectrum of a solid sample of **2** two intense ν(Mo–C) stretching modes are observed at 517 (A_1) and 497 cm^{-1} (E) in agreement with C_{3v} symmetry of the $N_3Mo(CO)_3$ core which should be compared with values 401 and 394 cm^{-1} reported for [Mo(CO)$_6$].[12] Thus the Mo–C bond is significantly stronger in **2** than in the hexacarbonylmolybdenum complex. Fig. 1 shows a correlation between the ν(CO) frequency (A_1) and the Mo–C bond distance for a series of molybdenum complexes with three amine nitrogen, three thioether sulfur,[8] three phosphane donor atoms[9] and [Mo(CO)$_6$].[10] This reflects the increasing π-acceptor ability of the respective ligand. The amine ligand L is a pure σ donor whereas thioethers, phosphanes and, ultimately, three additional carbonyl groups in [Mo(CO)$_6$] are increasingly stronger π acceptors. Spectroscopic and crystallographic data for complex **2** are very similar to those reported for [Mo(dien)-(CO)$_3$] (dien = diethylenetriamine) and, more recently, for two tripodal trisaminomethane complexes [Mo($C_{10}H_{19}N_3$)-(CO)$_3$].[11]

Oxidation of complexes **1** and **2** with thionyl chloride in CCl$_4$ under anaerobic conditions affords purple [CrLCl$_3$] **4** and yellow [MoLCl$_3$] **5** in essentially quantitative yields. This oxidative decarbonylation of [ML(CO)$_3$] species is a very useful synthetic route to complexes containing the LM fragment and a metal ion in a higher oxidation state.[6,7] From magnetic susceptibility measurements on solid samples of **4** and **5** in the temperature range 80–298 K using the Faraday method a temperature-independent magnetic moment of 3.8 μ_B for both species is calculated in excellent agreement with the expected spin-only value of 3.87 μ_B for octahedral d^3 complexes. The electronic spectrum of **5** in MeCN exhibits absorption maxima at 1053 (ε ≈1), 673 (≈7), 447 (130), 380 (220) and 252 nm (4600 dm^3 mol^{-1} cm^{-1}) in agreement with other octahedral molybdenum(III) complexes.[13] Complex **4** is insoluble in all common solvents; the solid-state reflection spectrum displays maxima at 720 (sh), 684 and 495 nm.

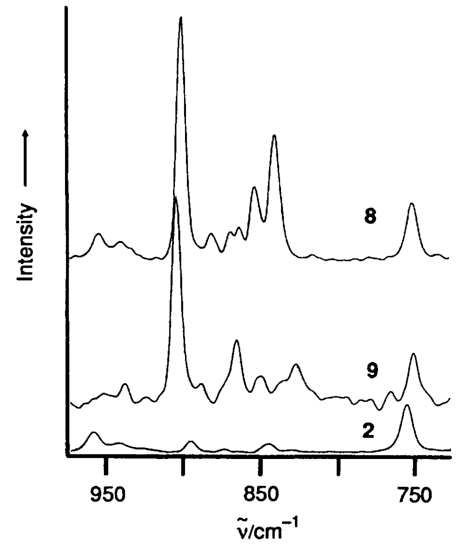

Fig. 2 Raman spectra of solid samples of complexes **2**, **8** and **9** in the region 720–990 cm^{-1}

The tribromo analogues [CrLBr$_3$] **6** and [MoLBr$_3$] **7** are obtained from the reaction of complexes **1** and **2** in CHCl$_3$ with bromine. Temperature-independent magnetic moments of 3.8 μ_B for **6** and 3.5 μ_B for **7** are again indicative of the d^3 electronic configuration of the respective metal ion. The electronic spectrum of **6** (MeCN) displays absorption maxima at 642 (ε = 70) and 455 (90), that of **7** (MeCN) at 691 (18), 461 (80) and 389 nm (180 dm^3 mol^{-1} cm^{-1}).

Complex **2** dissolved in 2.5 mol dm^{-3} nitric acid undergoes in the presence of air at 20 °C an exhaustive oxidation–decarbonylation reaction. Colourless microcrystals of [MoLO$_3$]·3H$_2$O **8** precipitate within 2 h. Complex **8** contains a molybdenum(VI) metal centre (d^0) and is diamagnetic. It is only sparingly soluble in water but beautiful colourless, cubic, single crystals suitable for X-ray structure analysis were grown from a hot aqueous solution by slow cooling to ambient temperature.

When a suspension of complex **8** in dry toluene is treated with 4 equivalents of phenyl isocyanate under anaerobic conditions at 70 °C a brown solid is obtained which may be recrystallized from MeCN yielding colourless crystals of [MoLO$_3$]·(PhNH)$_2$-CO **9**. Thus phenyl isocyanate has reacted with the water molecules of crystallization of **8** generating *N*,*N*′-diphenylurea.

The infrared and Raman spectra of solid samples of complexes **8** and **9** have been measured. The data are summarized in Table 2. According to Griffith and Wickin's analysis of the vibrational spectra of [Mo(dien)O$_3$][14] two Mo–O stretching modes $\nu_{sym}(A_1$, polarized in the Raman) and ν_{asym}(E, depolarized) are expected in C_{3v} local symmetry of the trioxomolybdenum(VI) moiety. The ν_{sym}(MoO$_3$) mode is observed as a fairly weak band in the infrared but strong band in the Raman spectrum at 903 and 907 cm^{-1} for **8** and **9**, respectively. The ν_{asym}(MoO$_3$) mode is intense in the infrared and weak in the Raman spectrum. In **8** and **9** the degeneracy of this mode (E) is lifted and two bands are observed both in the infrared and Raman spectrum. Fig. 2 shows the Raman spectra of solid samples of **2**, **8** and **9** in the region of the Mo=O stretching modes. We have included the spectrum of **2** in order to corroborate band assignments as MoO$_3$ modes which should not be present in the spectrum of **2**. Complexes **8** and **9** differ only by the nature, number and symmetry of hydrogen-bonding contacts of the terminal Mo=O groups. In **8** all three Mo=O groups are hydrogen bonded to a water molecule (C_3

Table 2 Vibrational spectroscopic data (cm^{-1}) for *cis*-trioxomolybdate(VI) complexes

	Infrared		Raman		
Complex	ν_{sym}(Mo–O), A_1	ν_{asym}(Mo–O), E	ν_{sym}(Mo–O), A_1	ν_{asym}(Mo–O), E	Ref.
8	904m^a	861, 846^a (vs)	903vs	857, 844 (m)	This work
	904m^b	860, 843^b (vs)			
9	907m	869, 826 (vs)	907vs	869, 832 (m)	This work
$[Mo\{HB(pz)_3\}O_3]^-$	898	845			15
$[Mo(dien)O_3]$	876	825	871	826	14
$[Mo(C_6H_2Me_3\text{-}2,4,6)O_3]^-$	920	880, 850			16
$[Mo(\eta^5\text{-}C_5Me_5)O_3]^-$	860	825			17

^{a} KBr disc. ^{b} In D_2O solution.

Table 3 Electronic and infrared spectroscopic data for vanadium complexes

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})^a	IR (cm^{-1})^b
10	760 (40), 510 (150)	
11	456 (3.7 × 10^3), 396 (2.4 × 10^3), 332 (8.5 × 10^3), 305 (7.1 × 10^3)	2050, 2080 ν(NCS)
12	765 (50), 570 (25), 465 (883)	2075, 2083 ν(NCS) 978 ν(V=O)

^{a} In MeCN solution. ^{b} KBr discs.

Table 4 Summary of electrochemical data^a

Complex	$E_{\frac{1}{2}}$^{b}/V	$E_{p,ox}$^{b}/V	$E_{p,red}$^{b}/V
1	+0.03 (r)	+0.89 (i)	
2	+0.34 (r)	+1.52 (i)	−0.08 (i)
3	+0.27 (r)	+1.36 (i)	−0.23 (i)
5	+1.02 (r)		
7	+1.085 (r)		
10^c	+1.31 (r)	−0.10 (i)	−0.92 (i)

r = Reversible, i = irreversible.

^{a} Conditions: MeCN; 0.10 mol dm^{-3} $[NBu_4]PF_6$; [complex] ≈ 10^{-3} mol dm^{-3}; platinum-button electrode, scan rate 20–200 mV s^{-1}; ferrocene internal standard. ^{b} Reference electrode Ag–AgCl (saturated LiCl, ethanol), *E*(ferrocene–ferrocenium) = 0.535 V *vs.* Ag–AgCl. ^{c} Solvent: CH_2Cl_2.

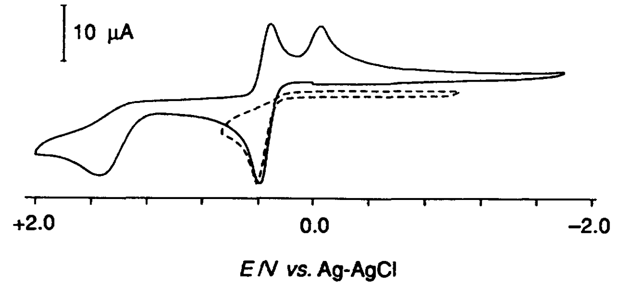

Fig. 3 Cyclic voltammograms of complex **2** in MeCN containing (*a*) 0.10 mol dm^{-3} $[NBu_4]PF_6$ (——) and (*b*) 0.10 mol dm^{-3} $[NBu_4]Br$ (– – – –) at a scan rate of 100 mV s^{-1} (platinum-button electrode)

symmetry) whereas in **9** only one Mo=O group forms two N–H···O contacts to the *N,N′*-diphenylurea and the other two are not involved in hydrogen bonding. The MoO_3 unit has C_s symmetry.

Previously we have reported the synthesis of analogous *fac*-MO_3 complexes containing the triamines 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane (M = Mo or W).[18–20]

Finally, we have briefly studied the reactivity of L toward VCl_3 dissolved in MeCN. From a solution of VCl_3 in dry MeCN under an argon blanketing atmosphere and reflux pink crystals of $[VLCl_3]$ **10** precipitate upon cooling of the solution. The chloro ligands in **10** are substitution labile and may be replaced by thiocyanate by dissolving **10** in water under anaerobic conditions and addition of NaSCN. Orange crystals of $[VL(NCS)_3]$ **11** precipitate. When the latter reaction is carried out in the presence of air the yellow vanadyl complex $[VOL(NCS)_2]$ **12** is obtained. Effective magnetic moments at 298 K of 2.7 μ_B for **10**, 2.6 μ_B for **11** and 1.8 μ_B for **12** agree well with spin-only values expected for octahedral vanadium-(III) (d^2) and -(IV) (d^1) complexes. Table 3 summarizes the electronic and infrared data. The corresponding complexes containing 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane have been reported previously.[21,22]

Electrochemistry.—Electrochemical data are summarized in Table 4. A representative cyclic voltammogram for the tricarbonylmetal complexes **2** and **3** is shown in Fig. 3 for **2** measured in MeCN using 0.10 mol dm^{-3} $[NBu_4]PF_6$ and $[NBu_4]Br$ as supporting electrolyte at a platinum-button electrode, respectively. The potential range −2.0 to +2.0 V *vs.* Ag–AgCl (saturated LiCl, EtOH) was scanned at scan rates 20–200 mV s^{-1}. In the absence of co-ordinating anions one reversible one-electron-transfer process occurs. Repetitive scans in the range 0.0–0.6 V *vs.* Ag–AgCl do not indicate a chemical reaction (decomposition) of the 17e species $[M^IL(CO)_3]^+$ under these conditions. We have previously shown that a similar species is chemically accessible. The complex $[MoL'(CO)_3]PF_6$ has been isolated and its crystal structure has been determined (L′ = 1,4,7-tribenzyl-1,4,7-triazacyclononane).[4] A second irreversible oxidation peak for **2** is observed at +1.5 V *vs.* Ag–AgCl which is accompanied by an irreversible reduction peak at −0.08 V *vs.* Ag–AgCl. This latter process is also observed for **3**. We propose that **2** and **3** undergo a two-electron oxidation with concomitant formation of a seven-co-ordinate species $[ML(CO)_3(MeCN)]^{2+}$ which at more negative potentials is reduced to the starting complex $[ML(CO)_3]$. Thus processes (1) and (2) are observed (M = Mo or W).

$$[M^0L(CO)_3] \rightleftharpoons [M^IL(CO)_3]^+ + e^- \quad (1)$$

$$[M^0L(CO)_3] + MeCN \rightleftharpoons [M^{II}L(CO)_3(MeCN)]^{2+} + 2e^- \quad (2)$$

If the cyclic voltammogram is recorded in the presence of the co-ordinating anion bromide (Fig. 3) only an irreversible two-electron oxidation peak at +0.38 V *vs.* Ag–AgCl is observed which we assign to the process (3). We have previously

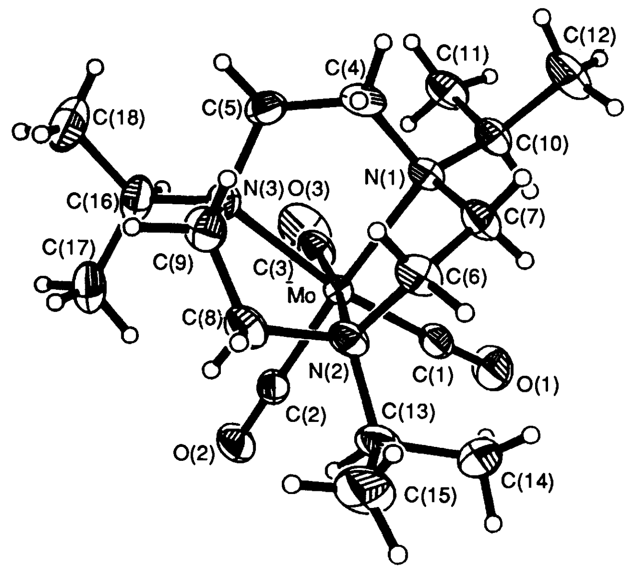

Fig. 4 Structure of the neutral molecule $[MoL(CO)_3]$ in crystals of complex **2** looking down a crystallographic C_3 axis

Table 5 Selected bond lengths (Å) and angles (°) for $[MoL(CO)_3]$ **2**

Mo–N(1)	2.360(2)	Mo–C(1)	1.914(3)
Mo–N(2)	2.371(2)	Mo–C(2)	1.921(3)
Mo–N(3)	2.377(2)	Mo–C(3)	1.920(3)
C(1)–O(1)	1.190(4)	C(2)–O(2)	1.178(3)
C(3)–O(3)	1.173(4)		
N(1)–Mo–C(1)	94.2(1)	N(2)–Mo–C(2)	97.0(1)
N(3)–Mo–C(3)	95.9(1)	N(1)–Mo–N(2)	76.7(1)
N(1)–Mo–N(3)	77.3(1)	N(2)–Mo–N(3)	76.7(1)
C(1)–Mo–C(2)	85.8(1)	C(2)–Mo–C(3)	82.7(1)
C(1)–Mo–C(3)	82.2(1)		

$$[M^0L(CO)_3] + Br^- \longrightarrow [M^{II}L(CO)_3Br]^+ + 2e^- \quad (3)$$

isolated such seven-co-ordinate species and determined the crystal structure of $[MoL''(CO)_3Br]ClO_4 \cdot H_2O$ (L″ = 1,4,7-triazacyclononane).[6]

The cyclic voltammogram of complex **1** in MeCN (0.10 mol dm^{-3} $[NBu_4]PF_6$) differs slightly from those of **2** and **3** due to the fact that the +II oxidation state is not as readily accessible. In addition to the reversible one-electron process (1) an irreversible three-electron oxidation peak is observed at +0.80 V *vs.* Ag–AgCl. The corresponding reduction peak is not observed in the scanned potential range −2.0 to +2.0 V *vs.* Ag–AgCl. We assign this irreversible oxidation to the formation of $[CrL(MeCN)_3]^{3+}$ with concomitant loss of carbonyl ligands.

In summary the electrochemistry of complexes **1**–**3** is very similar to that reported previously for other $[ML(CO)_3]$ species containing similar macrocyclic triamines L.[6,7]

The cyclic voltammograms of complexes **5** and **7** display one reversible one-electron transfer process, respectively. Coulometric measurements indicate that both species are reversibly oxidized according to equation (4) (X = Cl or Br). The complex

$$[Mo^{III}LX_3] \rightleftharpoons [Mo^{IV}LX_3]^+ + e^- \quad (4)$$

$[MoL''Br_3]PF_6$ has previously been isolated and structurally characterized.[7] Its redox potential is very similar to that measured for **7**.

Interestingly, the vanadium complex **10** is also reversibly oxidized to the corresponding $[VLCl_3]^+$ species and irreversibly reduced. The $[VLCl_3]^-$ species is not stable on the cyclovoltammetric time-scale (scan rate 100 mV s^{-1}).

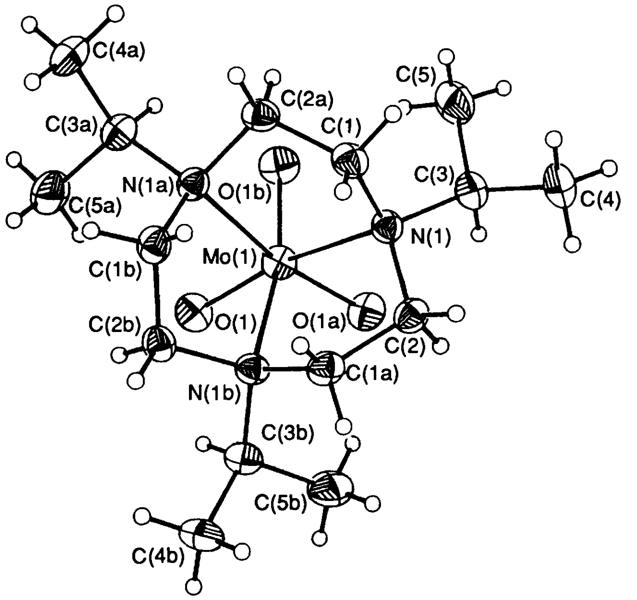

Fig. 5 Structure of the neutral molecule $[MoLO_3]$ in crystals of complex **8** looking down a crystallographic C_3 axis

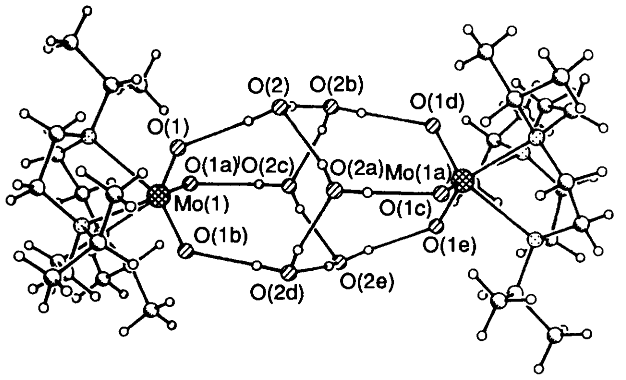

Fig. 6 Ball-and-stick representation of a dimeric unit $(MoOL_3)_2 \cdot (H_{12}O_6)$ in complex **8**

Crystal Structures of Complexes **2**, **8** *and* **9**.—The molecular structures of complexes **2**, **8** and **9** have been established by single-crystal X-ray analyses. That of **2** is shown in Fig. 4 and selected bond distances and angles are given in Table 5. Crystals of **2** consist of well separated neutral molecules $[MoL(CO)_3]$. Due to the steric requirements of the cyclic triamine the three carbonyl groups are facially co-ordinated. The quality of the crystals was excellent and, consequently, the positions of all hydrogen atoms were located and refined.

It is noted that the average Mo–C bond distance decreases as a function of decreasing π-acceptor ability of the donor atoms in *trans* position relative to the carbonyl groups. The average Mo–C bond length in **2** is the shortest at 1.918 Å, in the 1,4,7-trithiacyclononane analogue this distance is at 1.947 Å,[8] in the 1,5,9-triphosphacyclododecane complex it is 1.977 Å[9] and in $[Mo(CO)_6]$ a Mo–C distance of 2.06 Å has been reported.[23] As shown in Fig. 1 this distance correlates nicely with the ν(CO) stretching frequency (A_1). The nitrogen atoms in **2** are pure σ donors whereas the carbonyl group and phosphane ligand are π acceptors; the thioether ligand displays only moderate π-acceptor ability as has been proposed by Ashby and Lichtenberger.[8]

The neutral molecule in complex **2** does not possess crystallographically imposed symmetry, but it has nearly ideal C_3

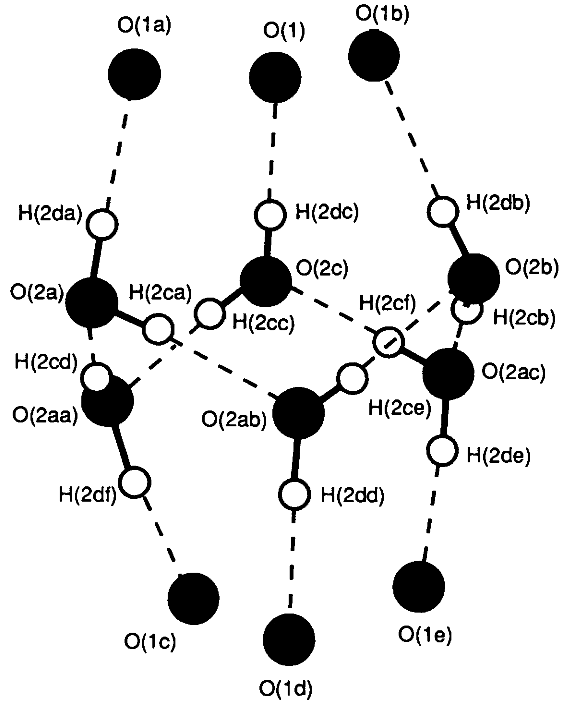

Fig. 7 Structure of the $(H_2O)_6$ unit between two $MoLO_3$ molecules in complex **8**

Table 6 Selected bond lengths (Å) and angles (°) for $[MoLO_3]\cdot 3H_2O$ **8**

Mo–O(1)	1.737(3)	N(1)–C(1)	1.488(5)
Mo–N(1)	2.438(3)	N(1)–C(2)	1.494(5)
C(1)–(C1A)	1.519(6)	N(1)–C(3)	1.534(5)
C(3)–C(4)	1.533(6)	C(3)–C(5)	1.520(6)
O(2)–H(2d)	0.86(4)	O(2)–H(2c)	0.78(5)
O(1)–Mo–N(1)	154.5(1)	N(1)–Mo–O(1B)	95.8(1)
O(1)–Mo–O(1A)	105.5(1)	N(1)–Mo–N(1A)	73.3(1)
N(1)–Mo–O(1A)	81.6(1)	N(2d)–O(2)–H(2c)	105(5)

symmetry. The three chelate rings, Mo–N–C–C–N, adopt the (λλλ) or (δδδ) conformation; both forms are present in the centrosymmetric space group. The racemate crystallizes. The isopropyl pendant arms adopt a conformation where the C–H vector is directed toward the neighbouring carbonyl group and the sterically more demanding methyl groups point as far away as possible from the CO ligands.

Fig. 5 displays the neutral molecule in complex **8**, Fig. 6 shows a ball-and-stick representation of a dimeric unit $(MoLO_3)_2(H_{12}O_6)$ and Fig. 7 shows the hexameric water unit between two $MoLO_3$ molecules. Table 6 summarizes the bond lengths and angles. Complex **8** crystallizes in the centrosymmetric cubic space group *Pa*3. The neutral complex lies on a crystallographic C_3 axis and the two $MoLO_3$ units in Fig. 6 are related by a crystallographic inversion centre. Thus both enantiomeric forms [(λλλ) and (δδδ)] of the co-ordinated tridentate amine are present in the crystal. Most interestingly the two $MoLO_3$ units are 'glued' together by six water molecules of crystallization which build a hydrogen-bonded cyclic water hexamer (Fig. 7). At each side of the water ring one face of an octahedral $MoLO_3$ unit is hydrogen-bonded *via* three terminal Mo=O groups to three axial hydrogen atoms of H_2O [O(1) ··· H(2d)–O(2c): O ··· O 2.797(3), O ··· H 1.94, H–O 0.86 Å; O–H ··· O 176°]. The puckered water ring is held together by an O(2a) ··· H(2c)–O(2c) hydrogen bond [O ··· O 2.787(3), H ··· O 2.015, H–O 0.78 Å]. This cyclic arrangement is closely related to the crystal structure of triethanolamine where six alcoholic ROH groups of two molecules form a very similar puckerering also with $\bar{3}$ symmetry in the solid state.[24] An isolated water tetramer has been characterized in crystals of $CF_3CO_2H\cdot H_2O$.[25] Crystals of **8** consist of $(MoLO_3)_2(H_{12}O_6)$ units which are held together by weak London forces. The three bulky isopropyl groups at each co-ordinated 1,4,7-triazacyclononane backbone prevent effectively the formation of more commonly observed sheets (two dimensional) or a three-dimensional network of water molecules of crystallization.

Table 7 Selected bond lengths (Å) and angles (°) for one independent molecule in crystals of $[MoLO_3]\cdot(PhNH)_2CO$ **9**

Mo–O(1)	1.730(3)	Mo–N(1)	2.447(4)
Mo–O(2)	1.754(3)	Mo–N(2)	2.414(4)
Mo–O(3)	1.726(3)	Mo–N(3)	2.454(4)
O(2) ··· N(7)	2.904(4)	O(2) ··· N(8)	2.820(4)
O(1)–Mo–O(2)	104.4(2)	O(1)–Mo–N(2)	96.4(1)
O(1)–Mo–O(3)	105.0(2)	O(2)–Mo–N(2)	154.9(1)
O(2)–Mo–O(3)	104.9(2)	O(3)–Mo–N(2)	82.6(1)
O(1)–Mo–N(1)	155.0(1)	N(1)–Mo–N(2)	73.8(1)
O(2)–Mo–N(1)	81.5(1)	O(1)–Mo–N(3)	82.0(1)
O(3)–Mo–N(1)	96.7(1)	O(2)–Mo–N(3)	95.5(1)
O(3)–Mo–N(3)	155.7(1)	N(1)–Mo–N(3)	73.2(1)
N(2)–Mo–N(3)	73.4(1)		

The ancillary ligand L enforces the *cis*-trioxo configuration in the neutral molecule $[MoLO_3]$. The bond distances and angles in the MoO_3 moiety are very similar to those in [Mo(dien)O_3][26] and $[NEt_4][Mo\{HB(pz)_3\}O_3]\cdot 2H_2O$[15] where pz is pyrazolyl. Interestingly, the geometry and metrical details of the MoO_3 unit in the four-co-ordinate anion mesityltrioxomolybdate(VI)[16] is also similar. In the particular, the Mo=O bond distances are short (1.73 ± 0.01 Å) and the O–Mo–O bond angles are obtuse (≈105°). The Mo=O bond distances in these structures are not significantly affected by the presence of hydrogen bonds to water molecules of crystallization. This is in contrast to the structure of the corresponding tungsten complex $[WO_3L']\cdot 3H_2O$[19] (L′ = 1,4,7-triazacyclononane) where one terminal oxo group forms a short hydrogen bond (W–O ··· OH_2) which leads to a significant elongation of the W–O bond (1.85 *vs.* 1.77 Å).

The average Mo–N bond distance in complex **8** is very long; these bonds are significantly weaker than those in [Mo(dien)O_3] and $[Mo\{HB(pz)_3\}O_3]$. They are also larger by 0.07 Å compared to those in **2** despite the fact that the ionic radius of a six-co-ordinate molybdenum(VI) ion is smaller than the radius of molybdenum(0). This is taken as a clear indication of a strong structural *trans* effect of the three terminal *cis*-oxo groups.

Crystals of complex **9** consist of hydrogen-bonded $[MoLO_3]\cdot(PhNH)_2CO$ moieties; there are two crystallographically independent sets of four such units per unit cell. The metrical details of these two sets (Table 7) are very similar and we will discuss only one of these. Fig. 8 shows one independent unit. The neutral molecule, *N*,*N*′-diphenylurea is bound to one terminal oxo group of the $MoLO_3$ moiety *via* two weak O ··· H–N hydrogen bonds. The O ··· H–N distances at 2.904(4) and 2.820(4) Å clearly indicate this type of interaction although the protons have not been located. A consequence of this hydrogen bonding is that the local symmetry of the MoO_3 moiety is lowered from C_{3v} to C_s with two shorter Mo–O distances at 1.727(3) and one longer Mo=O bond at 1.754(3) Å.

Experimental

Materials and Methods.—All solvents were dried over appropriate reagents and distilled prior to use. All chemicals were purchased from commercial sources and used as supplied. Proton NMR spectra were recorded on a Bruker WP 80 instrument at 20 °C using deuteriated solvents as lock and reference [$SiMe_4$ (δ 0)], infrared spectra on a Perkin Elmer FT

Table 8 Crystal data and data collection parameters * for the structures of [MoL(CO)$_3$] **2**, [MoLO$_3$]·3H$_2$O **8** and [MoLO$_3$]·(PhNH)$_2$CO **9**

	2	**8**	**9**
Molecular formula	$C_{18}H_{33}MoN_3O_3$	$C_{15}H_{39}MoN_3O_6$	$C_{28}H_{45}MoN_5O_4$
M	435.4	453.4	611.6
Crystal system	Monoclinic	Cubic	Monoclinic
Crystal colour, habit	Pale yellow prisms	Colourless cubes	Colourless prisms
Crystal size/mm	0.46 × 0.43 × 0.40	0.17 × 0.23 × 0.27	0.35 × 0.60 × 0.85
Space group	$P2_1/n$	$Pa3$	$P2_1/c$
a/Å	8.576(2)	16.110(5)	13.365(7)
b/Å	16.428(3)		19.790(9)
c/Å	14.770(3)		23.372(6)
β/°	100.61(3)		104.26(3)
U/Å^3	2045.3(7)	4181.1(6)	5991.3(7)
Z	4	8	8
D_c/g cm^{-3}	1.41	1.44	1.36
F(000)	912	1920	2576
μ(Mo-Kα)/mm^{-1}	0.64	0.64	0.46
Diffractometer	Siemens P4	Syntex R3	Syntex R3
2θ range/°	3–55	3–53	3–53
Reflections measured	5176	3535	13 079
Independent reflections (R_{int})	4687 (0.0146)	3535 (0.027)	13 079 (0.023)
Observed reflections (criterion)	3242 [$F > 6.0\sigma(F)$]	887 [$I \geqslant 2.5\sigma(I)$]	8244 [$I \geqslant 2.5\sigma(I)$]
Least-squares parameters	358	98	692
R	0.026	0.039	0.052
R'	0.029	0.030	0.044
Largest difference peak, hole/e Å^{-3}	0.31, −0.49	0.40, −0.32	0.42, −0.52
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.000\,2F^2$	$\sigma^2(F)$	$\sigma^2(F)$

* Details in common: T = 298 K, Mo-Kα radiation (λ = 0.710 73 Å), ω scan mode; absorption correction, empirical ψ scans of seven reflections.

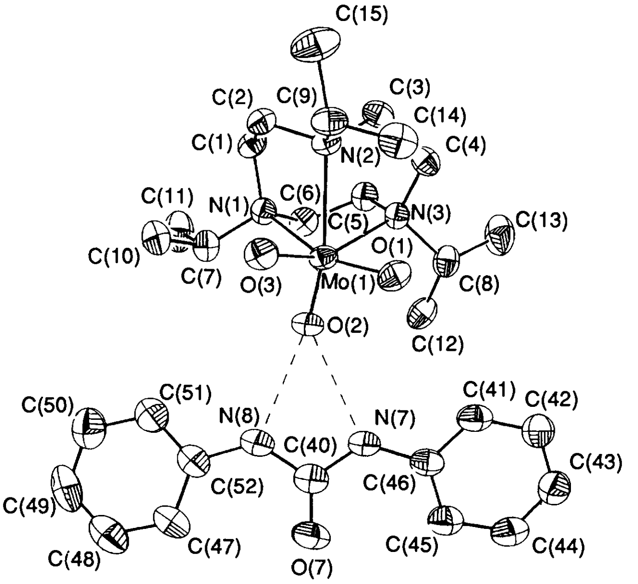

Fig. 8 Structure of one crystallographically independent unit [MoLO$_3$]·(PhNH)$_2$CO in crystals of complex **9**

Table 9 Atomic coordinates (× 10^4) for compound **2**

Atom	x	y	z
Mo	2580(1)	2457(1)	2402(1)
C(1)	2839(3)	3248(2)	3369(2)
C(2)	4345(3)	1906(2)	3139(2)
C(3)	4232(3)	3085(2)	2019(2)
O(1)	3072(3)	3768(1)	3939(2)
O(2)	5462(3)	1599(1)	3595(2)
N(1)	223(2)	3046(1)	1588(1)
N(2)	575(3)	1562(1)	2715(2)
N(3)	2012(3)	1642(2)	1052(2)
O(3)	5281(3)	3467(2)	1828(2)
C(4)	−177(4)	2673(2)	650(2)
C(8)	853(4)	813(2)	2197(2)
C(6)	−1030(3)	1909(2)	2348(2)
C(5)	1183(4)	2239(2)	355(2)
C(7)	−969(3)	2810(2)	2158(2)
C(9)	918(4)	960(2)	1195(2)
C(10)	282(3)	3974(2)	1546(2)
C(17)	4397(6)	715(3)	1360(3)
C(13)	730(4)	1347(2)	3731(2)
C(16)	3463(4)	1329(2)	703(2)
C(11)	1403(4)	4273(2)	936(3)
C(12)	−1338(5)	4374(2)	1238(3)
C(14)	416(5)	2072(3)	4313(3)
C(15)	−313(6)	635(3)	3921(3)
C(18)	3115(8)	971(3)	−269(3)

spectrometer 1720X as KBr discs, electronic absorption spectra on a Perkin Elmer Lambda 9 UV/VIS/NIR spectrophotometer in the range 200–1000 mm and Raman spectra on solid samples on a Perkin Elmer FT-IR 1760X model with additional FT-Raman 1700X equipment using a Nd YAG laser (1064 nm, output 0.4 W). Temperature-dependent magnetic susceptibilities were measured in the range 80–298 K by using the Faraday method. Corrections for underlying diamagnetism of solid samples were applied with use of Pascal's constants. Cyclic voltammograms were recorded on PAR equipment consisting of a model 173/179 potentiostat/galvanostat and model 175 universal programmer.

Synthesis of the Ligand 1,4,7-*Triisopropyl*-1,4,7-*triazacyclononane* (L).—To a toluene solution (50 cm^3) of 1,4,7-triazacyclononane (10 g, 77 mmol) was added isopropyl bromide (32 g, 260 mmol). The solution was stirred at 80–90 °C for 2–3 h. During the reaction a yellowish, oily mass separated. After addition of KOH (15 g) the mixture was stirred at 80–90 °C for 5 h. The precipitated KBr was filtered off and the filtrate extracted three times with toluene. The solvent was removed from the combined extracts by rotary evaporation. The resulting mixture of mono-, di- and tri-substituted 1,4,7-triazacyclononane derivatives was dissolved in methanol (150 cm^3) and solid NaClO$_4$ (10 g) was added with vigorous stirring. Water was added in small amounts to the clear solution until it remained turbid. After a few hours the monohydroperchlorate of the desired ligand, [HL]ClO$_4$ precipitated as colourless crystals (yield ≈25 g).

The free base was obtained by dissolving [HL]ClO$_4$ (25 g) in toluene (100 cm^3) and addition of powdered KOH (25 g). The solution was stirred at 20 °C for 18 h after which time the residue ($KClO_4$) was filtered off. After drying over $MgSO_4$ the solvent was removed by rotary evaporation. The ligand is a colourless oil at room temperature (yield: 13 g; 66% based on starting material 1,4,7-triazacyclononane).

Preparation of Complexes.—The tricarbonyl complexes [ML(CO)$_3$] (M = Cr **1**, Mo **2** or W **3**) were obtained in excellent yields (>95%) by reaction of the respective hexacarbonyl [M(CO)$_6$] (10 mmol) and the ligand L (10 mmol) dissolved in mesitylene (150 cm^3) under an argon blanketing atmosphere with heating under reflux for 3 h. During the reaction yellowish precipitates formed which were filtered off. The complexes are air-stable and may be stored for months without detectable decomposition.

Table 10 Atomic coordinates (× 10^4) for compound **8**

Atom	*x*	*y*	*z*
Mo(1)	1418(1)	1418(1)	1418(1)
O(1)	454(2)	1209(2)	1854(2)
N(1)	2876(2)	1822(2)	1456(2)
C(1)	2983(3)	2734(3)	1554(3)
C(2)	3211(3)	1367(3)	2191(3)
C(3)	3324(3)	1493(3)	682(3)
C(4)	4273(2)	1519(3)	747(3)
C(5)	3051(3)	1936(3)	−105(3)
O(2)	3622(3)	4212(2)	94(2)

[CrLCl$_3$] **4** *and* [MoLCl$_3$] **5**. To a solution of complex **1** or **2** (1.0 mmol) in CCl_4 (20 cm^3) under an argon atmosphere was added dropwise thionyl chloride (4 cm^3) with stirring. The solution was heated to reflux until the CO evolution ceased and a purple (Cr) or yellow (Mo) suspension was obtained. The solids were filtered off (yields: **4**, 96; **5**, 74%).

[CrLBr$_3$] **6** *and* [MoLBr$_3$] **7**. To a suspension of complex **1** or **2** (1.0 mmol) in $CHCl_3$ (20 cm^3) was added dropwise bromine (0.30 g). The solution was stirred at 20 °C until the CO evolution ceased and a green (Cr) or orange (Mo) precipitate had formed (yields: **6**, 87; **7**, 68%).

[MoLO$_3$]·3H_2O **8** and [MoLO$_3$]·(PhNH)$_2$CO **9**. Complex **2** (0.44 g, 1.0 mmol) was dissolved in 2.5 mol dm^{-3} nitric acid (10 cm^3) in an open vessel in the presence of air. From the clear colourless solution a white precipitate formed slowly which was filtered off. The material was recrystallized from the minimum amount of hot (90 °C) water by slow cooling to room temperature (yield: 0.20 g; 44%). The resulting complex **8** (0.20 g) was suspended in dry toluene (20 cm^3) and phenyl isocyanate (0.20 g, 1.8 mmol) was added dropwise. After heating the suspension at 70 °C for 5 h a brown precipitate formed which was filtered off and recrystallized from MeCN. Colourless crystals of complex **9** in 41% (0.22 g) yield were obtained.

[VLCl$_3$] **10**, [VL(NCS)$_3$] **11** *and* [VOL(NCS)$_2$] **12**. A suspension of VCl_3 (0.79 g, 5.0 mmol) in dry MeCN (20 cm^3) was heated to reflux under an argon atmosphere. To the mixture was added the ligand L (1.28 g, 5.0 mmol) dissolved in MeCN (5.0 cm^3). After heating to reflux for 30 min a pink precipitate of complex **10** formed upon cooling of the solution to 20 °C. Yield: 1.88 g, 91%. To an aqueous solution (10 cm^3) of NaSCN (1.0 g)

Table 11 Atomic coordinates (× 10^4) for compound **9**

Atom	*x*	*y*	*z*
Mo(1)	2 144(1)	156(1)	3 166(1)
O(1)	1 920(2)	−39(2)	3 845(1)
O(2)	1 669(2)	−544(2)	2 722(1)
O(3)	1 293(2)	803(2)	2 892(1)
N(1)	3 196(3)	270(2)	2 450(2)
N(2)	3 312(3)	1 084(2)	3 505(2)
N(3)	3 832(3)	−345(2)	3 619(2)
C(1)	3 827(3)	904(2)	2 554(2)
C(2)	3 442(3)	1 403(2)	2 943(2)
C(3)	4 319(3)	859(2)	3 876(2)
C(4)	4 284(3)	141(2)	4 096(2)
C(5)	4 490(3)	−401(2)	3 189(2)
C(6)	3 872(3)	−340(2)	2 557(2)
C(7)	2 524(4)	228(3)	1 828(2)
C(8)	3 706(4)	−1 024(2)	3 900(2)
C(9)	2 806(4)	1 620(2)	3 820(2)
C(10)	1 818(4)	839(3)	1 657(2)
C(11)	3 117(4)	125(3)	1 355(2)
C(12)	3 297(4)	−1 574(2)	3 446(2)
C(13)	4 684(4)	−1 285(3)	4 329(2)
C(14)	2 636(4)	1 359(2)	4 399(2)
C(15)	3 394(4)	2 289(2)	3 923(3)
Mo(2)	7 246(1)	1 364(1)	3 359(1)
O(4)	7 269(2)	1 635(2)	4 063(1)
O(5)	6 647(2)	2 020(2)	2 896(1)
O(6)	6 365(2)	710(2)	3 221(1)
N(4)	7 992(3)	1 138(2)	2 530(2)
N(5)	8 431(3)	434(2)	3 653(2)
N(6)	8 974(3)	1 848(2)	3 612(2)
C(21)	8 604(3)	497(2)	2 614(2)
C(22)	8 373(4)	56(2)	3 089(2)
C(23)	9 502(3)	663(2)	3 915(2)
C(24)	9 546(3)	1 400(2)	4 088(2)
C(25)	9 456(3)	1 844(2)	3 099(2)
C(26)	8 671(4)	1 734(2)	2 519(2)
C(27)	7 161(4)	1 143(3)	1 958(2)
C(28)	8 047(4)	−45(2)	4 068(2)
C(29)	8 979(4)	2 556(2)	3 869(2)
C(30)	7 561(5)	1 193(3)	1 399(2)
C(31)	6 440(4)	538(3)	1 898(2)
C(32)	8 639(5)	−712(3)	4 177(3)
C(33)	8 065(5)	286(3)	4 656(2)
C(34)	10 064(4)	2 814(3)	4 172(2)
C(35)	8 438(4)	3 066(2)	3 407(2)
N(7)	233(3)	8 536(2)	3 069(2)
N(8)	−352(2)	9 025(2)	2 178(2)
O(7)	−1 185(3)	8 101(2)	2 417(2)
C(40)	−500(4)	8 517(3)	2 546(2)
C(41)	1 119(4)	8 261(3)	4 056(2)
C(42)	1 382(4)	7 827(3)	4 530(2)
C(43)	913(5)	7 211(3)	4 504(3)
C(44)	183(4)	7 036(3)	4 009(3)
C(45)	−91(4)	7 453(3)	3 518(2)
C(46)	397(4)	8 072(3)	3 539(2)
C(47)	−1 897(4)	8 926(3)	1 356(2)
C(48)	−2 371(5)	9 094(3)	787(3)
C(49)	−1 939(6)	9 520(3)	456(3)
C(50)	−972(5)	9 787(3)	713(3)
C(51)	−474(5)	9 610(3)	1 285(3)
C(52)	−928(4)	9 176(3)	1 605(2)
N(9)	4 653(3)	8 034(2)	1 809(2)
N(10)	5 253(3)	7 637(2)	2 742(2)
O(8)	6 080(3)	8 517(2)	2 423(2)
C(60)	5 386(4)	8 104(2)	2 327(2)
C(61)	3 804(4)	8 184(3)	801(2)
C(62)	3 640(5)	8 528(3)	276(3)
C(63)	4 213(5)	9 086(3)	227(3)
C(64)	4 967(5)	9 287(3)	699(3)
C(65)	5 144(4)	8 951(3)	1 231(2)
C(66)	4 552(4)	8 403(2)	1 285(2)
C(67)	5 522(4)	7 111(3)	3 688(2)
C(68)	6 129(5)	6 945(3)	4 234(2)
C(69)	7 135(5)	7 161(3)	4 420(3)
C(70)	7 510(4)	7 544(3)	4 037(3)
C(71)	6 919(4)	7 721(3)	3 478(2)
C(72)	5 910(4)	7 504(2)	3 304(2)

Table 12 Microanalytical data for complexes of 1,4,7-triisopropyl-1,4,7-triazacyclononane

	Analysis* (%)		
Complex	C	H	N
1 $C_{18}H_{33}CrN_3O_3$	55.3 (55.2)	8.6 (8.5)	10.7 (10.7)
2 $C_{18}H_{33}MoN_3O_3$	49.7 (49.7)	7.9 (7.7)	9.7 (9.7)
3 $C_{18}H_{33}N_3O_3W$	40.7 (40.6)	6.1 (6.2)	7.9 (7.9)
4 $C_{15}H_{33}Cl_3CrN_3$	43.3 (43.5)	7.9 (8.0)	10.3 (10.1)
5 $C_{15}H_{33}Cl_3MoN_3$	39.3 (39.4)	7.2 (7.3)	9.2 (9.2)
6 $C_{15}H_{33}Br_3CrN_3$	32.8 (32.9)	6.3 (6.1)	7.9 (7.7)
7 $C_{15}H_{33}Br_3MoN_3$	30.4 (30.5)	5.7 (5.6)	7.0 (7.1)
8 $C_{15}H_{39}MoN_3O_6$	39.4 (39.7)	8.8 (8.7)	9.2 (9.3)
9 $C_{28}H_{45}MoN_5O_4$	54.5 (54.9)	7.5 (7.4)	11.3 (11.5)
10 $C_{15}H_{33}Cl_3N_3V$	42.1 (43.6)	5.8 (6.1)	9.9 (10.2)
11 $C_{18}H_{33}N_6S_3V$	44.6 (45.0)	6.5 (6.9)	17.3 (17.5)
12 $C_{17}H_{33}N_5OS_2V$	46.5 (46.6)	7.5 (7.6)	16.0 (16.0)

* Required values are given in parentheses.

was added **10** (0.2 g, 0.5 mmol) under an argon atmosphere with stirring at 20 °C. After 30 min an orange precipitate of **11** formed which was filtered off. Yield: 0.22 g (91%). When the above reaction was carried out in the presence of air under otherwise identical conditions yellow microcrystals of **12** were obtained in 59% yield.

Microanalytical data for the new complexes are given in Table 12.

Crystal Structure Analysis of Complexes **2**, **8** *and* **9**.—Table 8 summarizes the relevant data for the crystal structure analyses. Final atom coordinates for the three structures are presented in Tables 9–11. Intensity data were corrected for Lorentz, polarization and absorption effects (ψ scans) in the usual manner. The structures were solved by conventional Patterson and Fourier difference methods using the SHELXTL-PLUS program package.[27] The function minimized during full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F)$. Neutral-atom scattering factors and anomalous dispersion correction for non-hydrogen atoms were taken from ref. 28. The positions of the hydrogen atoms in **2** were located in the final Fourier difference map and included in the refinement with variable positional parameters and variable isotropic thermal parameters. Found C–H bond distances in the range 0.92–1.05 Å are considered chemically reasonable. The H atoms in **8** were located and refined with variable positional parameters and a fixed isotropic parameter $U = 0.080$ Å^2 (methylene, methine groups and water molecule of crystallization) whereas the positions of the protons of the methyl groups were calculated (riding model). In **9** the hydrogen atoms were placed in calculated positions with a fixed isotropic thermal parameter ($U = 0.080$ Å^2). All other atoms were refined with anisotropic thermal parameters.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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