Synthesis and Characterization of 3,6-Bis(3,5-dimethylpyrazol-1-yl)pyridazine (L) Derivatives of Mononuclear Manganese(I) and Group 6 Metal(O) Carbonyl Complexes. Crystal and Molecular Structures of $[M(CO)_4L]$ (M = Cr or Mo)†

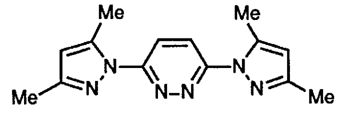
M. Pilar Gamasa,[a] **José Gimeno,***[,a] **Elena Lastra,**[a] **Santiago García-Granda**[b] **and Dámaso Moreiras**[c]
[a] *Departamento de Química Organometálica*
[b] *Departamento de Química Física y Analítica*
[c] *Departamento de Geología, Universidad de Oviedo, 33071 Oviedo, Spain*

Treatment of $[M(CO)_6]$ (M = Cr, Mo or W) or $[MnBr(CO)_5]$ with 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine (L) in refluxing tetrahydrofuran or toluene (M = Cr or W) gives, respectively, $[M(CO)_4L]$ and $[MnBr(CO)_3L]$. Infrared and ^1H NMR spectra indicate that the tetradentate heterocycle acts only as a monochelate ligand forming mononuclear complexes. The crystal structures of $[M(CO)_4L]$ (M = Cr or Mo) have been determined by X-ray diffraction. Crystals are isotypic, monoclinic, space group $P2_1/c$, with $Z = 4$ in unit cells of dimensions $a = 8.0790(1)$, $b = 19.5539(2)$, $c = 12.5186(1)$ Å, $\beta = 91.598(1)°$ (M = Cr) and $a = 8.081(1)$, $b = 19.793(2)$, $c = 12.607(6)$ Å, $\beta = 91.62(3)°$ (M = Mo). The structures have been solved by Patterson methods and DIRDIF. Final conventional agreement factors were $R = 0.043$, $R' = 0.038$ for M = Cr and $R = 0.051$, $R' = 0.038$ for M = Mo. The structures consist of distorted octahedral arrangements with four carbonyl groups and two nitrogen atoms of the ligand L around each metal atom, and the unco-ordinated nitrogen atom of the pyrazolyl group twisted by almost 180° with respect to the corresponding one in the co-ordinated ring. The ligand, which is almost planar, forms a monochelate ring with small bite angles N–M–N 75.2(1) and 71.0(3)° for Cr and Mo respectively. Deviation from the linearity of the mutually *trans*-carbonyl groups is revealed by the C–M–C bond angles of 166.7(2) (M = Cr) and 167.0(6)° (M = Mo) with slighter distortions of the mutually *cis*-carbonyl groups [range 84(1)–87(1)°]. Cyclic voltammetric studies in CH_2Cl_2 show single non-reversible redox waves in accord with the observed energies of the metal-to-ligand charge transfer absorptions in the electronic spectra.

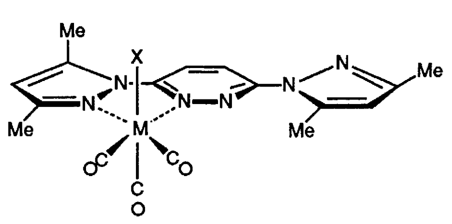
N,N′-Chelating biheteroaromatic ligands have been extensively used in co-ordination chemistry, especially those which are able to form five-membered metallacycles.[1] Heterocycles containing two azole components belong to this class of ligands showing versatile properties in respect of the formation of polynuclear complexes.[2] In this field we have reported[3] the synthesis of homo and hetero bi- or poly-nuclear complexes using 2,2′-biimidazole (H_2bim) and their derivatives as mono- or di-anionic ligands.

We now report the reactivity of a triheteroaromatic ligand, namely 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine (L), towards the Group 6 metal hexacarbonyls and $[MnBr(CO)_5]$. To the best of our knowledge the only known metal carbonyl derivatives containing L are limited to a few mononuclear rhodium(I) complexes.[4] Recent studies[5] have shown the ability of this and similar diazine ligands to generate predominantly binuclear transition-metal complexes. On the other hand, there is current interest in the co-ordination chemistry of these types of ligands with delocalized π systems, as potential electron-transmitting groups with special redox and photocatalytic properties.[6]

As we described in this work, reactions of L with $[M(CO)_6]$ (M = Cr, Mo or W) and $[MnBr(CO)_5]$ only led to the formation of mononuclear tetracarbonyl derivatives, $[M(CO)_4L]$ or the tricarbonyl $[MnBr(CO)_3L]$. The behaviour of L contrasts with the ability of related tetradentate ligands *e.g.* 2,5-bis-(2-pyridyl)pyrazine (L′), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (L″) and 2,3-bis(2-pyridyl)pyrazine (L‴) which are able to form binuclear Group 6 metal(O) tetracarbonyl complexes containing a bis-chelating ligand.[6]



L



M	X
Cr	CO
Mo	CO
W	CO
Mn	Br

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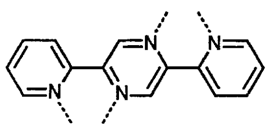
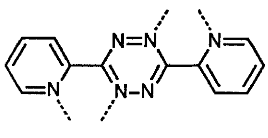
† [3,6-Bis(3,5-dimethylpyrazol-1-yl-κ$N^{2'}$)pyridazine-κN^2]-tetracarbonyl-chromium and -molybdenum.

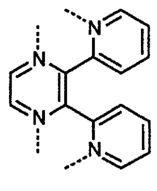
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



L′



L″



L‴

Experimental

Instrumentation.—NMR spectra were recorded on a Varian FT80 spectrometer at 79.54 MHz using $SiMe_4$ as internal standard; IR spectra on a Perkin-Elmer 1720-X FT in CH_2Cl_2 or KBr and ultraviolet–visible spectra on a Perkin-Elmer Lambda 3A in CH_2Cl_2. Cyclic voltammetry was performed with a Metrohm VA 611 potentiostat using a platinum working electrode and a saturated calomel reference electrode (SCE). Solutions (0.1 mol dm^{-3}) of tetrabutylammonium hexafluorophosphate in dry dichloromethane were used as electrolyte. The concentration of the complexes during measurements was about 10^{-3} mol dm^{-3}; scan rate 200 mV s^{-1}. The C, H and N analyses were carried out with a Perkin-Elmer 240 B microanalyser.

Synthesis.—The synthesis of the ligand L has been reported previously[7] but we followed the modified method by Thompson *et al.*[8] The compound [MnBr(CO)$_5$] was prepared as described elsewhere.[9] All reactions and measurements were carried out under nitrogen and the solvents were dried before use by standard methods. The identity and purity of the novel complexes were established by spectroscopy and correct elemental C, H and N analyses.

[M(CO)$_4$L] (M = Cr, Mo *or* W). *General procedure.* An equimolar mixture of [M(CO)$_6$] and L (1 mmol) was dissolved in tetrahydrofuran (thf) (M = Mo) or toluene (M = Cr or W) (40 cm^3) and heated under reflux until the ν(CO) absorption of [M(CO)$_6$] was no longer present in the IR spectra (M = Cr, 3; Mo, 3; W, 12 h). After filtration the resulting dark violet solution was concentrated (10 cm^3) and hexane added (20 cm^3) to give the desired compound as a crystalline solid. Yields (%) and colours: M = Cr, 70, violet; M = Mo, 84, dark red; M = W, 70, purple (Found: C, 49.9; H, 3.9; N, 19.6. Calc. for $C_{18}H_{16}CrN_6O_4$: C, 50.0; H, 3.7; N, 19.4. Found: C, 45.0; H, 3.3; N, 17.5. Calc. for $C_{18}H_{16}MoN_6O_4$: C, 45.4; H, 3.4; N, 17.6. Found: C, 38.9; H, 3.1; N, 14.8. Calc. for $C_{18}H_{16}N_6O_4W$: C, 38.3; H, 2.8; N, 14.9%). IR(KBr): ν(L) M = Cr, 1452s, 1447s, 1427m, 1382m, 1079s, 670m, 650m, 607m and 560m; M = Mo, 1452s, 1447s, 1427s, 1382m, 1072m, 842m, 652w, 607w and 402w; M = W, 1586s, 1575s, 1550s, 1464m, 1439m, 1382s, 1346s, 1278m, 1263m, 1147w, 1117w, 1069m, 1051m, 988m, 971m, 833m, 626m and 559m cm^{-1}.

[MnBr(CO)$_3$L]. An equimolar mixture of [MnBr(CO)$_5$] and L (1 mmol) was dissolved in thf (40 cm^3) and heated under reflux for 0.5 h. Working up as described above yielded an orange crystalline solid (84%) (Found: C, 40.9; H, 3.3; N, 17.5. Calc. for $C_{17}H_{16}BrMnN_6O_3$: C, 41.9; H, 3.3; N, 17.3%). IR(KBr): ν(L) 1447s, 1442s, 1367s, 1102m, 997m, 842m, 677m, 627m and 392w cm^{-1}.

Crystallographic Data Collection, Resolution and Refinement of the Structures of [M(CO)$_4$L] (M = Cr *or* Mo).—Experimental data for both structures are collected in Table 3. The data were collected at 293 K on an Enraf-Nonius CAD4 single-crystal diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) and graphite-crystal monochromator. Unit-cell dimensions were determined from the angular settings of 25 reflections with $25 < \theta < 30°$ for M = Cr and $20 < \theta < 30°$ for M = Mo. The space group was determined from systematic absences. The ω–2θ scan technique was used, with a variable scan rate and a maximum scan time of 60 s per reflection. The intensity was checked by monitoring three standard reflections every 60 min. Drift corrections were applied. Profile analysis[10,11] was performed on all reflections. An empirical absorption correction was applied, using ψ scans[12] (correction factors range from 0.97 to 1.00 for M = Cr and 0.97 to 1.00 for M = Mo).

Both structures were solved by the Patterson method using the program SHELX 86[13] (followed by DIRDIF[14] for M = Mo) and Fourier synthesis. Isotropic least-squares refinements were performed using SHELX.[15] For M = Cr this refinement converged to $R = 0.079$ and at this stage further absorption corrections were applied using DIFABS.[16] For M = Mo isotropic least-squares refinements converged to $R = 0.077$. Further anisotropic refinements followed by a Fourier difference synthesis allowed the location of most hydrogen atom in both compounds. Positional and anisotropic thermal parameters of the non-hydrogen atoms were refined. Some of the hydrogen atoms were geometrically placed and their overall isotropic thermal parameters fixed at 0.08 Å^2. For the rest of the hydrogen atoms, positional parameters and isotropic thermal parameters were refined. The function $\Sigma w(F_o - F_c)^2$ was minimized, where $w = 1/[\sigma^2(F_o) + gF_o^2)$ and $\sigma(F_o)$ was obtained from counting statistics (g is given in Table 3). The atomic scattering factors were taken from ref. 17. The structures were drawn with the PLUTO program,[18] and the geometrical calculations were made with PARST.[19]

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

Results and Discussion

Synthesis.—Mononuclear complexes [M(CO)$_4$L] (M = Cr, Mo or W) were obtained in good yields (70–90%) by heating under reflux a solution in toluene (M = Cr or W) or thf (M = Mo) containing an equimolar mixture of [M(CO)$_6$] and the ligand. The reactions proceeded slowly with evolution of CO and were monitored by IR spectroscopy, checking the ν(CO) absorption band of [M(CO)$_6$]. After *ca.* 3 h this band had completely disappeared. The complexes can be crystallized by adding hexane to the filtered and concentrated solutions. The complex *fac*-[MnBr(CO)$_3$L] was similarly obtained from [MnBr(CO)$_5$] and L using refluxing tetrahydrofuran as solvent.

Attempts to obtain binuclear derivatives have been unsuccessful. Reactions of [M(CO)$_6$] with L in 2:1 molar ratio in refluxing thf, toluene or with ultraviolet irradiation led only to the mononuclear complexes. Prolonged treatments resulted in decomposition.

The novel carbonyl derivatives were isolated as air-stable red-violet (M = Cr, Mo or W) or orange (M = Mn) crystalline solids and characterized by elemental analyses, IR and proton NMR spectroscopy (Tables 1 and 2). X-Ray crystal structure determinations of [Mo(CO)$_4$L] (M = Cr or Mo) (see below) confirm the proposed structures.

Infrared and ^{1}H *NMR Spectra.*—The IR spectra of solutions of complexes [M(CO)$_4$L] in dichloromethane (Table 1) exhibit the four ν(CO) absorption bands ($2A_1 + B_1 + B_2$) expected for octahedral *cis*-tetracarbonylmetal complexes with C_{2v} symmetry as is also found[6] for the analogous tetracarbonyl derivatives [M(CO)$_4$L″] [M = Cr, Mo or W; L″ = 3,6-bis-(2-pyridyl)-1,2,4,5-tetrazine]. The corresponding spectrum of the complex [Mn(CO)$_3$L] shows three ν(CO) absorption bands ($2A' + A''$) typical of the *fac*-tricarbonyl arrangement in octahedral complexes of the type *fac*-[MnBr(CO)$_3$(L–L)] where L–L = chelate ligand.[20]

Table 1 Infrared,[a] electrochemical[b] and m.l.c.t. absorption[c] data for the new complexes

Complex	ν(CO)/cm^{-1}				E_{ox}/V	E_{red}/V	λ(m.l.c.t.)/ nm
	A_1(m)	B_1(s)	A_1(sh)	B_2(s)			
[Cr(CO)$_4$L]	2009	1897	1882	1839	+0.5	−1.48	509 (3.7)
[Mo(CO)$_4$L]	2004	1902	1882	1834	+0.68	−1.57	474 (3.6)
[W(CO)$_4$L]	2008	1890	1883	1838	+0.67	−1.50	485 (3.6)
	A′(s)	A′(m)	A″(m)				
[MnBr(CO)$_3$L]	2034	1947	1922		+1.12	−1.40	426 (3.5)

[a] In CH_2Cl_2 solution; for ν(L) absorptions in KBr see Experimental section. [b] 0.1 mol dm^{-3} [NBu_4]PF_6 as supporting electrolyte in CH_2Cl_2. Platinum electrode *vs.* SCE; potential range −1.6 to +1.5 V; irreversible waves; scan rate 200 mV s^{-1}. [c] In CH_2Cl_2 solutions (log ε in parentheses).

Table 2 Proton NMR chemical shifts * (δ) of the carbonyl complexes and free L

Compound	$H_{a,b}$	$^2J(H^aH^b)$/Hz	$H_{a,b}$(pz)	$Me_{a,b}$	$Me_{a',b'}$
L	8.20(s)		5.99(s)	2.29(s)	2.72(s)
[Cr(CO)$_4$L]	8.14(d)	7.8	6.18(s)	2.51(s)	2.80(s)
	7.69(d)		5.91(s)	2.25(s)	2.61(s)
[Mo(CO)$_4$L]	8.28(d)	8	6.23(s)	2.52(s)	2.84(s)
	7.81(d)		6.03(s)	2.27(s)	2.71(s)
[W(CO)$_4$L]	8.30(d)	9.6	6.25(s)	2.52(s)	2.80(s)
	7.78(d)		6.02(s)	2.19(s)	2.71(s)
[MnBr(CO)$_3$L]	8.34(d)	8	6.23(s)	2.64(br s)	2.78(s)
	7.86(d)		6.03(s)	2.23(s)	2.64(br s)

* At 79.54 Hz in $CDCl_3$, relative to $SiMe_4$; s = singlet, d = doublet and br = broad.

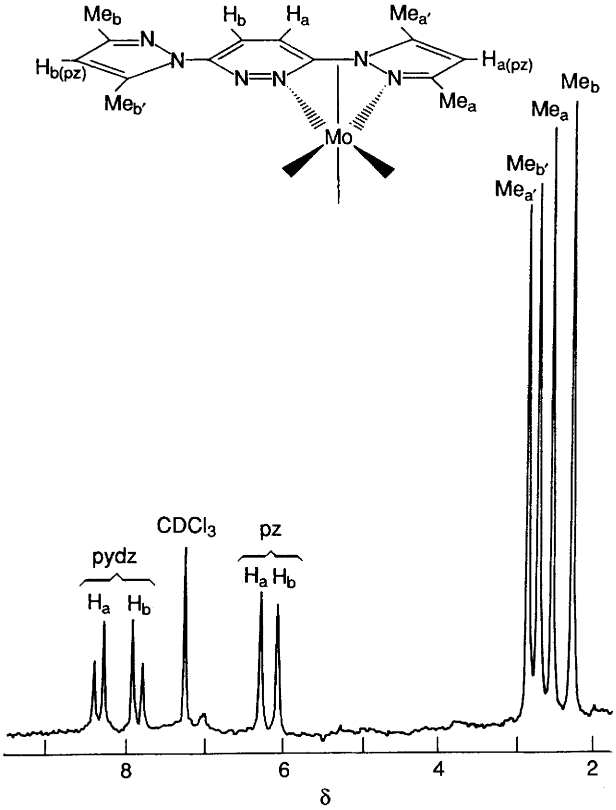


Fig. 1 Proton NMR spectrum ($CDCl_3$) of [Mo(CO)$_4$L]

Table 3 Crystal data for [M(CO)$_4$L] *

	M = Cr	M = Mo
Crystal colour	Violet	Red
Crystal size/mm	0.20 × 0.13 × 0.08	0.24 × 0.07 × 0.03
a/Å	8.0790(1)	8.081(1)
b/Å	19.5539(2)	19.793(2)
c/Å	12.5186(1)	12.607(6)
β/°	91.598(1)	91.62(3)
U/Å^3	1976.87(8)	2016(1)
D_c/Mg m^{-3}	1.45	1.57
μ(Mo-Kα)/cm^{-1}	5.99	6.69
Drift correction range	0.99–1.06	0.94–1.01
h,k,l range	−11,−27,0 to 11,8,17	−11,−27,0 to 11,27,17
Number of measured reflections	8645	12 231
Number of unique reflections	5778	5873
R_{int} (for some double measured)	0.042	0.048
Observed reflections	1671 [$I > 3\sigma(I)$]	1176 [$I > 2\sigma(I)$]
Number of refined parameters	299	293
R, *R′*	0.043, 0.038	0.051, 0.038
g Value	0.002	0.0002
Maximum shift/e.s.d.	0.09	0.07
Final peak in Fourier difference synthesis (e Å^{-3})		
Maximum	0.27	0.57
Minimum	−0.25	−0.50

* Details in common: prismatic; space group $P2_1/c$; $Z = 4$; θ 0–30°.

Proton NMR spectra (Table 2) show evidence of the ligand monochelate co-ordination and the mononuclear nature of the complexes in which the corresponding pyridazine protons become chemically inequivalent. Significantly, the spectrum of [Mo(CO)$_4$L] (Fig. 1) shows four methyl resonances attributable to the chemical inequivalence of the four methyl groups, in accord with the presence of one unco-ordinated pyrazolyl moiety. Pyridazine (pydz) and pyrazolyl (pz) protons also become inequivalent, showing the typical pattern of an AB spin system and two single signals, respectively. The signals were assigned according to the established[21] resonances for L and analogous heterocyclic systems. In general, the signals of protons closer to the co-ordinated nitrogen atoms, *i.e.* Me_a, $Me_{a'}$, H_a(pz), are shifted to lower fields while the rest remain approximately unchanged compared with the free ligand.

Description of the Crystal Structures of [M(CO)$_4$L] (M = Cr *or* Mo).—Fig. 2 shows a view of the chromium complex, with the atom labelling scheme. The co-ordination for the molyb-

Table 4 Fractional positional parameters for [Cr(CO)$_4$L] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr	0.100 84(10)	0.106 96(4)	0.256 11(6)	C(5)	0.232 6(6)	−0.042 1(3)	0.496 3(4)
O(1)	0.236 4(5)	0.243 9(2)	0.314 1(3)	C(6)	0.322 8(6)	−0.006 7(3)	0.570 0(4)
O(2)	−0.006 2(5)	0.163 9(2)	0.043 7(3)	C(7)	0.345 1(5)	0.063 1(3)	0.552 6(4)
O(3)	−0.219 0(5)	0.170 3(2)	0.324 4(3)	C(8)	0.477 0(6)	0.170 8(3)	0.628 2(4)
O(4)	0.429 7(6)	0.090 1(2)	0.146 4(4)	C(9)	0.561 5(7)	0.180 2(4)	0.722 6(5)
N(1)	0.068 6(4)	−0.037 4(2)	0.328 0(3)	C(10)	0.569 8(6)	0.117 9(3)	0.774 7(4)
N(2)	0.011 1(5)	0.007 4(2)	0.247 0(3)	C(11)	0.033 8(9)	−0.161 2(3)	0.385 9(6)
N(3)	0.189 8(4)	0.060 1(2)	0.395 7(3)	C(12)	−0.186 1(6)	−0.002 0(3)	0.093 3(4)
N(4)	0.281 8(4)	0.095 6(2)	0.469 1(3)	C(13)	0.434 6(7)	0.221 4(3)	0.542 2(5)
N(5)	0.437 5(4)	0.102 5(2)	0.626 5(3)	C(14)	0.648 8(7)	0.100 8(3)	0.880 5(4)
N(6)	0.495 6(5)	0.069 4(2)	0.717 3(3)	C(15)	0.184 9(6)	0.189 8(3)	0.292 2(4)
C(1)	0.001 5(5)	−0.102 2(3)	0.315 5(4)	C(16)	0.032 5(7)	0.139 6(3)	0.126 5(4)
C(2)	0.096 4(7)	−0.098 1(3)	0.226 3(4)	C(17)	−0.097 4(8)	0.141 8(3)	0.303 0(4)
C(3)	−0.090 8(6)	−0.031 2(3)	0.187 0(4)	C(18)	0.305 9(7)	0.090 6(3)	0.190 0(4)
C(4)	0.166 8(5)	−0.007 2(2)	0.409 1(3)				

Table 5 Fractional positional parameters for [Mo(CO)$_4$L] with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	0.103 6(1)	0.110 32(6)	0.254 03(9)	C(5)	0.230(2)	−0.044 1(7)	0.498(1)
O(1)	0.250(1)	0.249 4(5)	0.318 0(8)	C(6)	0.323(2)	−0.009 7(7)	0.573(1)
O(2)	−0.005(1)	0.168 4(5)	0.035 0(8)	C(7)	0.347(1)	0.058 6(7)	0.555 9(9)
O(3)	−0.234(1)	0.175 9(6)	0.324 9(10)	C(8)	0.482(2)	0.164 7(7)	0.630(1)
O(4)	0.447(1)	0.093 0(6)	0.143 7(9)	C(9)	0.565(2)	0.172 2(9)	0.724(1)
N(1)	0.067(1)	−0.038 5(4)	0.331 4(7)	C(10)	0.572(2)	0.110(1)	0.776 8(9)
N(2)	0.013(1)	0.003 9(4)	0.249 7(8)	C(11)	0.034(2)	−0.161 0(6)	0.389(1)
N(3)	0.192(1)	0.057 3(5)	0.401 6(7)	C(12)	−0.184(2)	−0.006 1(7)	0.096(1)
N(4)	0.284(1)	0.091 7(4)	0.474 6(8)	C(13)	0.446(2)	0.216 0(6)	0.548(1)
N(5)	0.442(1)	0.097 3(5)	0.629 2(7)	C(14)	0.651(2)	0.095 4(8)	0.887(1)
N(6)	0.495(1)	0.064 4(5)	0.719 0(9)	C(15)	0.197(2)	0.197 0(6)	0.293(1)
C(1)	0.002(1)	−0.103 3(6)	0.319 8(9)	C(16)	0.030(2)	0.145 5(7)	0.118(1)
C(2)	−0.094(2)	−0.098 8(6)	0.229(1)	C(17)	−0.117(2)	0.148 9(7)	0.306(1)
C(3)	−0.089(2)	−0.033 7(6)	0.189(1)	C(18)	0.322(2)	0.093 3(7)	0.188(1)
C(4)	0.168(1)	−0.008 6(6)	0.412 6(9)				

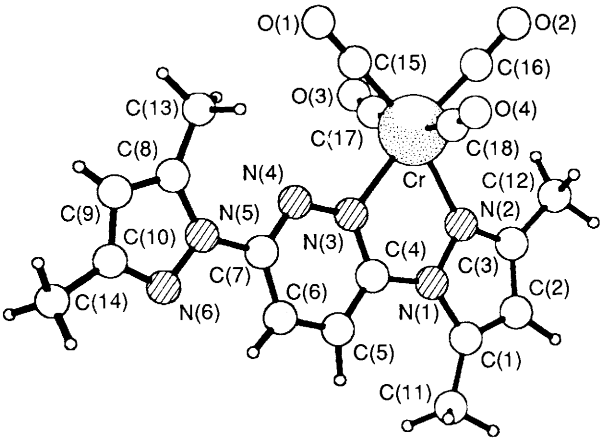


Fig. 2 A view of the chromium complex showing the co-ordination and labelling scheme

denum complex is identical and follows a similar numbering scheme. Final atomic positional parameters are given in Tables 4 and 5, selected bond lengths and angles in Table 6.

The structures are isotypic and show pseudo-octahedral arrangements around the metal atoms, each of them bonded to four carbonyl groups and two nitrogen atoms from L. Thus, the ligand only uses two of the four nitrogen atoms (one from a pyrazolyl group and the other from the pyridazine moiety), acting as a typical bidentate chelate ligand and forming a five-membered N,N metallocycle.

The octahedral arrangements are clearly distorted as is shown by the deviation from the linearity of the *trans*-carbonyl groups with bond angles C(17)–M–C(18) of 166.7(2) (M = Cr) and 167.0(6)° (M = Mo). Slight distortions are also observed for the mutually *cis*-carbonyl groups (*cis* C–M–C bond angles) and for the corresponding *cis* C–M–N angles with values in the range respectively of 84.1(6)–87.0(6) and 93.8(2)–103.0(5)°. The N–M–N bond angles 75.2(1) (M = Cr) and 71.0(3)° (M = Mo) show the small bite angle of the ligand, similar to that found for 2,2′-bipyridyl (bipy) carbonylmolybdenum complexes [Mo(CO)$_2$(bipy)$_2$] (73.6°)[22] and [Mo(CO)$_3$(bipy)(py)] (py = pyridine).[23]

The two pyrazole rings form angles of 6.1(1) and 3.9(1)°, for M = Cr and 5.2(4) and 4.5(4)° for M = Mo with respect to the pyridazine ring. These values are similar to that of 6.2° reported[24] for the canted angle of the pyrazole rings with respect to the pyridazine ring in the dinuclear copper(II) compound [Cu$_2$L(μ-OH)Cl$_2$]$^+$. The Mo–N distances, 2.23(1) Å (average), are in the range of those previously observed for [Mo(CO)$_2$(bipy)$_2$][22] and [Mo(CO)$_3$(bipy)(py)][23] (bipy *trans* to carbonyl groups). The Cr–N distances are shorter, 2.08(1) Å (average), as expected for the smaller size of the metal atom. The metal–carbon bond lengths, 1.93(1)–2.06(2) Å (M = Mo) and 1.809(5)–1.900(6) Å (M = Cr), can be compared with averages for molybdenum(0) or chromium(0) complexes, *e.g.* [Mo(CO)$_6$] [Mo–C 2.06(2)],[25] [Mo(CO)$_3$(bipy)(py)] [Mo–C 1.96(2)],[23] [Mo(CO)$_2$(bipy)$_2$] [Mo–C 1.93(1)],[22] [Cr(CO)$_6$] [Cr–C 1.915][26] and [Cr(CO)$_4$(tmen)] (tmen = Me$_2$NCH$_2$CH$_2$NMe$_2$) (Cr–C 1.866 Å).[27]

Moreover the Mo–C or Cr–C bond lengths involving CO groups *trans* to nitrogen atoms are significantly shorter than those *cis* to them. This seems to indicate a more favourable M(d$_\pi$) $\longrightarrow$ CO(π^*) back bonding for the CO groups *trans* to the N–N chelate ring, compared with that of CO mutually *trans* (*cis* to the ring), as a consequence of the M(d$_\pi$) $\longrightarrow$ L(π^*) back bonding which is weaker than M(d$_\pi$) $\longrightarrow$ CO(π^*).

Table 6 Selected distances (Å) and angles (°) relevant to the chromium and molybdenum co-ordination spheres with e.s.d.s in parentheses

	M = Cr	M = Mo
M–N(2)	2.080(4)	2.232(9)
M–N(3)	2.083(3)	2.336(8)
M–C(15)	1.809(5)	1.932(1)
M–C(16)	1.816(5)	1.928(1)
M–C(17)	1.851(6)	2.059(2)
M–C(18)	1.900(6)	2.003(2)
N(2)–M–N(3)	75.2(1)	71.0(3)
N(2)–M–C(15)	168.5(2)	166.0(5)
N(2)–M–C(16)	100.6(2)	103.0(5)
N(2)–M–C(17)	93.4(2)	94.1(5)
N(2)–M–C(18)	97.2(2)	97.2(5)
N(3)–M–C(15)	93.8(2)	95.2(5)
N(3)–M–C(16)	173.6(2)	172.9(5)
N(3)–M–C(17)	100.2(2)	100.0(5)
N(3)–M–C(18)	90.4(4)	90.0(5)
C(15)–M–C(16)	90.6(2)	90.9(5)
C(15)–M–C(17)	85.0(2)	85.7(6)
C(15)–M–C(18)	86.2(2)	85.0(6)
C(16)–M–C(17)	84.8(2)	84.1(6)
C(16)–M–C(18)	85.2(2)	87.0(6)
C(17)–M–C(18)	166.7(2)	167.0(6)
O(1)–C(15)–M	178.5(5)	178.6(1.2)
O(2)–C(16)–M	176.2(5)	175.5(1.2)
O(3)–C(17)–M	171.8(5)	171.7(1.3)
O(4)–C(18)–M	170.5(5)	169.8(1.3)

Finally it is worth considering in more detail the significant deviation from linearity of the *trans*-carbonyl groups giving rise to a pseudo-octahedral six-co-ordination around the metal atoms. Since apparently there are no steric requirements, this must be attributed to electronic reasons. This explanation has been proposed by Kubacek and Hoffmann[28] who have studied theoretically the deformations from octahedral geometry in molybdenum and other transition-metal carbonyl complexes, although these studies have focused on d^4 metal ions. The distortions shown by the d^6 chromium and molybdenum complexes are comparable to those in the calculated most favourable structure for $[MoCl_2(CO)_2(PH_3)_2]$ where the two *trans*-phosphine ligands subtend an angle of 170° about the metal (towards the CO groups) with slighter deviations from 90° of the bond angles formed by ligands in *cis* positions. In the present cases the electronic properties and the small bite angle of the ligand L must enforce a shift from the idealized octahedral situation to a more energetically favourable structure in agreement with the theoretical analysis of the molecular distortion. However, it should be kept in mind that the model complexes studied are d^4 compared with present d^6 which could result in additional effects.

Electrochemical Studies and Electronic Spectra.—Electrochemical measurements on the carbonyl complexes by cyclic voltammetry (platinum electrode) in dichloromethane solutions (*vs.* the saturated calomel electrode) show for each complex one irreversible oxidation wave as well as one reduction wave, also irreversible. The values are collected in Table 1 and were measured between -1.6 and $+1.5$ V. Although no coulometric measurements were carried out, one-electron redox processes may take place by analogy with related tetracarbonyl complexes.[29]

The observed irreversibility of the oxidation processes at the metal centre is probably based on the lability of the oxidized species, the ions d^5 Cr^I, Mo^I and W^I, as is well known for molybdenum and tungsten tetracarbonyl complexes.[29] The greater oxidation potentials observed for the molybdenum and tungsten compared with the chromium analogue indicate a stronger destabilization of the highest occupied molecular orbital (HOMO) in the latter complex as is also shown by the metal-to-ligand charge-transfer (m.l.c.t.) transition energies determined from the electronic spectra (see below). Comparison of oxidation potentials for tetracarbonyl complexes shows that the E° values follow a similar trend to that observed by others[30] for $[M(CO)_4(L\text{–}L)]$ complexes for which, in general, the values increase from chromium to molybdenum but this increase does not extend to tungsten.

Electronic spectra of the complexes (CH_2Cl_2 solutions) in the visible region (see Table 1) show one absorption band assigned to metal d to ligand π^* charge-transfer transition (m.l.c.t.) on the basis of their absorption coefficients ($\varepsilon > 1000$ dm^3 mol^{-1} cm^{-1}) with a wavelength sequence such as Mo < W < Cr (spectrum of free ligand shows a strong absorption in the UV region below 400 nm). In agreement with previous observations[6] the chromium complexes display the lowest m.l.c.t. transition energies because the metal-centred HOMO is most destabilized in $Cr(CO)_4$ complexes.[29]

The energy values of these transitions compare reasonably well with those observed for analogous tetracarbonyl complexes containing N–N chelate ligands.[6,31] Although these absorption bands can comprise several transitions from filled d levels to the unoccupied lowest π^* orbital of the ligand, a similar trend of metal oxidation ability can be deduced from electrochemical measurements and electronic spectra.

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