Crystal Structure Studies of Hydrazido(2−)quinolin-8-olato-complexes of Molybdenum and Tungsten

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Crystalline samples of five complexes of the formula [M(NNH$_2$)(quin)(PMe$_2$Ph)$_3$]X, where quin = quinolin-8-olate, M = Mo or W, X = I, Br, or Cl, have been examined by *X*-ray diffraction methods to observe structural differences which would account for differences in protonation reaction products. From complete analyses of three crystals, with (M,X) = (W,I), (Mo,I), and (Mo,Br), the metal, in the cationic complex, is found in almost identical octahedrally co-ordinated environments. In each case, the M–N–N system is linear and the hydrazido-hydrogen atoms are both strongly hydrogen-bonded to anions. Differences are found in (i) the extended hydrogen-bonding schemes, (ii) the position of one of the anions with respect to the cation, and (iii) the orientations of the substituted phosphine ligands.

IN the investigations into the reduction of the ligated nitrogen in dinitrogen complexes of molybdenum and tungsten, stable intermediate complexes containing the hydrazido(2—)-ligand have been identified.[1]

The proportions and yields of ammonia and hydrazine produced from complexes with dinitrogen or hydrazido-(2—)-ligands appear to depend on the metal, the reagent, the solvent, and the nature of other ligands in the complexes.[1,2] Until recently,[2,†] ammonia was the principal product in almost all reactions examined; the first major exceptions were found in a study of some of the compounds [M(NNH$_2$)(quin)(PMe$_2$Ph)$_3$]X, where quin = quinolin-8-olate, M = Mo or W, and X = Cl, Br, or I.

These complexes were prepared by treatment of [MX$_2$(NNH$_2$)(PMe$_2$Ph)$_3$] with an excess of quinolin-8-ol.[3] On reaction with an excess of H$_2$SO$_4$ in methanol, *in vacuo*, the molybdenum compounds gave only ammonia, but the tungsten compounds yielded hydrazine, exclusively for the compounds with X = Br and I, and as the major product for X = Cl (a small amount of NH$_3$ was detected here).

Crystalline samples of a number of the quinolin-8-olato-complexes were submitted for analysis by *X*-ray diffraction methods to try to identify, in the crystal form of these compounds, structural differences which might account for the different reduction products. A brief report on the crystal structure of the two iodides (M = Mo and W; X = I) has been published;[4] fuller details of the analyses of these and of other members of the series are now presented.

EXPERIMENTAL

Five samples with the formula [M(NNH$_2$)(quin)(PMe$_2$Ph)$_3$]X have been examined, (1; M = W, X = I. 2; M = Mo, X = I. 3; M = Mo, X = Br. 4; M = W, X = Cl. 5; M = Mo, X = Cl).

Crystals of (5) appear as deep reddish purple flaky plates. *X*-Ray photographs indicate that these ' crystals ' are accumulations of microcrystalline particles; the photographs were primarily of powder rings with some small discrete spots on the rings. No suitable single crystals were found.

The very deep purple-red crystals of (4) showed either very diffuse spots or long streaks on their *X*-ray photographs. A crystal suitable for diffractometer examination could not be found.

X-Ray photographs of the three remaining samples, (1), (2), and (3) showed more promise, and after space groups and approximate cell dimensions had been determined, crystals of each were mounted on our Enraf-Nonius CAD4 diffractometer for measurement of more precise cell dimensions and of diffraction intensities (Table 1).

TABLE 1

Details of diffractometer measurements [a]

	Complex		
	(1)	(2)	(3)
(*a*) Determination of accurate cell parameters			
No of reflections whose centred settings were used in the refinement	25	23	24
Range of θ (°) of these reflections	15—17.5	12—16	12—13.5
(*b*) Measurements of diffraction intensities, by the variable scan speed technique, using parameters optimized from analyses of peak shapes			
Maximum time per reflection (s)	100	100	90
Goniometer (ω): detector scan speed ratio	1 : 1	3 : 5	3 : 5
ω scan angle, DOMA (°) [b]	0.7	0.8	0.5
No. of intensity control reflections	3	3	2
Crystal deterioration (fall in control intensities)	*ca.* 8%	Nil	Nil
Maximum θ value (°)	17.5	22	25
No. of independent reflections	2 493	4 328	3 164
No. of ' observed ' reflections [$I > n\sigma(I)$] [c]	2 206	3 629	2 614
n	2	2	1

[a] Radiation (for each crystal) = monochromated Mo-K_α, λ(Mo-K_α) = 0.710 69 Å. [b] Total scan angle, $\Delta\omega = \frac{3}{2}$ (DOMA + 0.35 tanθ). [c] $I = T - 2(b_1 + b_2)$ and $\sigma(I) = \sqrt{T + 4(b_1 + b_2) + pI^2}$, where T is the scan count through the reflection (the central $\frac{2}{3}$ of the scan), b_1 and b_2 are background measurements over the outer $\frac{1}{6}$ of the scan, each side of the peak, and p is a factor (0.000 9) to reduce the weights of the largest intensity reflections.

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† We suspect, from the molecular geometry, that the crystal structure described in ref. 2 is of a hydrazido(2—)-hydrido-complex of tungsten, [WClBr(NNH$_2$)H(PMe$_2$Ph)$_3$]Br.

Crystal Data.—(1). $C_{33}H_{41}IN_3OP_3W\cdot 0.5C_9H_7NO$, M = 972.0, Orthorhombic, space group $Pbcn$ (no. 60), a = 18.889(2), b = 23.013(2), c = 18.106(2) Å, U = 7 870 Å^3, F(000) = 3 824, μ(Mo-K_α) = 39.3 cm^{-1}, D_m = 1.64 (by flotation), Z = 8, D_c = 1.64 g cm^{-3}. Crystals are deep purple; one was dissolved to an approximately spherical shape, diameter 0.27 mm, for analysis.

(2). $C_{33}H_{41}IMoN_3OP_3$, M = 811.5, Monoclinic, space group $P2_1/c$ (no. 14), a = 15.749(1), b = 13.012(1), c = 17.776(1) Å, β = 103.377(5)°, U = 3 544 Å^3, F(000) = 1 632, μ(Mo-K_α) = 13.85 cm^{-1}, D_m = 1.51 (by flotation), Z = 4, D_c = 1.52 g cm^{-3}. Crystals are deep red; a rectangular plate 0.55 × 0.47 × 0.12 mm was selected for analysis.

(3). $C_{33}H_{41}BrMoN_3OP_3$, M = 764.5, Monoclinic, space group Aa (variation of no. 9), confirmed by the X-ray structure analysis, a = 10.700(2), b = 32.876(6), c = 11.118(3) Å, β = 113.52(2)°, U = 3 586 Å^3, F(000) = 1 560, μ(Mo-K_α) = 16.2 cm^{-1}, Z = 4, D_c = 1.416 g cm^{-3}. Crystals are deep carmine and slightly air-sensitive. A small plate, 0.20 × 0.15 × 0.08 mm, was selected for analysis.

TABLE 2

Details of least-squares refinement [a]

		Complex		
		(1)	(2)	(3)
(*a*) Atoms with anisotropic temperature factors [b]		W, I, P, N [c]	Mo, I, P, N [c]	Mo, Br
(*b*) Hydrazido-hydrogen atoms	co-ordinates	Independent	Independent	Independent
	$U_{iso.}$	Fixed at 0.05 Å^2	Tied, refined	Independent
(*c*) Other hydrogen atoms				
Fixed C–H distances (Å)		1.08	0.96	1.08
Of quinolin-8-olato-ligand	co-ordinates	Riding [d]	Riding	Riding
	$U_{iso.}$	Independent	Tied to one refined value	Riding
Of phenyl rings	co-ordinates	Part of rigid body	Riding	Riding
	$U_{iso.}$	Tied to one refined value/ring	Tied to one refined value/ring	Riding
Of methyl groups	co-ordinates	Part of CH_3 rigid group, pivoting about *C* atom	Riding in staggered form	Riding in staggered form
	$U_{iso.}$	Tied to single refined value	Tied to single refined value	Riding
Weighting scheme, w		c (constant)	c	$[\sigma(F)^2 + 0.000\,576\,F^2]^{-1}$
No. of reflections used		2 206	3 629	2 614
R		0.0338	0.0387	0.0541
R'		0.0336	0.0373	0.0595

[a] All non-hydrogen atoms were refined independently, except the C atoms of the phenyl rings in the phosphine groups of (1), where regular hexagons of carbon atoms were refined as rigid bodies, pivoting about C(1). [b] All other atoms were refined with isotropic thermal parameters, $U_{iso.}$. [c] N atoms of hydrazido-ligand only. [d] Parameters (co-ordinates or $U_{iso.}$) described as 'riding' were tied to those of the bonded carbon atom.

In the processing of the diffractometer data, Lorentz and polarisation factors were applied; for complex (1), a factor to allow for crystal deterioration was included. No absorption corrections were made. Structure amplitudes were then derived.

Each structure was determined by the heavy-atom method. The metal atoms and the cations were located from Patterson syntheses, and the lighter atoms found in electron-density and difference maps. In (1), a molecule of quinolin-8-ol was also found, disordered about a two-fold symmetry axis; the atoms of this molecule have not been completely resolved.

The details of the least-squares refinement (Table 2) varied considerably for the three structures, depending on (i) the number and quality of 'observed' intensity data, (ii) the computing facilities available at the time, and (iii) the experimentor. In each structure, one of the critical hydrogen atoms (of the hydrazido-group) was located in a Fourier-difference map; the co-ordinates of the second hydrogen atom of this group were calculated and both atoms were included in the refinement process. The refined parameters of these atoms must be used with caution, and due regard should be taken of their estimated standard deviations (e.s.d.s). Co-ordinates of all other hydrogen atoms were calculated and their treatment is summarised in Table 2.

Analytical scattering factor curves and anomalous scattering factors for W, Mo^{3+}, I$^-$, Br$^-$, and O$^-$ were taken from ref. 5; for the remaining atoms, the values incorporated in the refinement program, SHELX,[6] were used.

Results of the refinement of (3) in the alternative polar cell (*i.e.* with signs of all co-ordinates reversed) were examined; corresponding final R and R' values were 0.058 7 and 0.067 6 for the 2 614 reflections, and e.s.d.s of all parameters were higher. We conclude that the correct polar direction of the crystal selected is defined by the co-ordinates quoted in this paper in the normal right-handed axial system.

Atomic parameters of the three complexes are in Tables 3–5. Listings of measured and calculated structure factors have been deposited in Supplementary Publication No. SUP 22889 (57 pp.).*

Computing.—The diffractometer intensity data were processed in the program CAD4.[7] The program SHELX [6] was used for the analysis and refinement of each structure. The diagrams were taken from ORTEP [8] plots. These three programs have been adapted for the ICL System 4 at this Station. Molecular geometries were calculated with programs of our X-RAY ARC library [9] for the IBM 1130 computer.

RESULTS AND DISCUSSION

Views of the three cationic complexes and their neighbouring anions are in Figure 1. The positions of

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

hydrogen atoms of all the methyl groups were not refined freely and must be considered suspect; these atoms were not included in any geometrical calculations.

The metal atoms in the three structures are octahedrally co-ordinated and have very similar environments; co-ordination dimensions are in Tables 6 (bond

TABLE 3

Atomic parameters for (1) with estimated standard deviations in parentheses

(*a*) Co-ordinates (fractional $\times 10^4$) and isotropic thermal parameters, $U_{iso.}$ (10^3 Å^2)

Atom[a]	x	y	z	$U_{iso.}$
W	3 137.3(2)	2 671.7(2)	879.0(3)	
I(1)[b]	5 000	4 109(1)	2 500	
I(2)[b]	5 000	1 494(1)	2 500	
N(1)	3 218(5)	1 741(4)	645(5)	45(3)
C(2)	3 561(6)	1 335(5)	1 023(6)	47(3)
C(3)	3 531(6)	739(5)	841(7)	57(4)
C(4)	3 115(6)	571(6)	264(7)	63(4)
C(4A)	2 726(6)	975(5)	−140(6)	51(3)
C(5)	2 251(6)	842(6)	−727(7)	65(4)
C(6)	1 919(7)	1 277(5)	−1 080(7)	69(4)
C(7)	2 006(6)	1 861(5)	−907(7)	58(4)
C(8)	2 456(6)	2 006(5)	−325(6)	49(3)
C(8A)	2 802(6)	1 564(5)	54(6)	43(3)
O(8)	2 576(4)	2 549(3)	−108(4)	58(2)
N(2)	3 600(5)	2 735(4)	1 715(5)	
N(3)	3 901(8)	2 772(5)	2 395(9)	
H(3A)	4 072(60)	3 095(43)	2 419(70)	50
H(3B)	3 987(74)	2 491(47)	2 495(83)	50
P(1)	4 264(2)	2 751(1)	144(2)	
C(11)	4 566(5)	3 390(3)	−327(5)	58(4)
C(12)	4 299(5)	3 509(3)	−1 029(5)	113(6)
C(13)	4 497(5)	4 017(3)	−1 395(5)	137(7)
C(14)	4 961(5)	4 407(3)	−1 058(5)	111(5)
C(15)	5 227(5)	4 288(3)	−355(5)	110(5)
C(16)	5 030(5)	3 780(3)	10(5)	84(4)
C(17)	4 997(7)	2 565(6)	738(7)	85(4)
C(18)	4 318(8)	2 198(6)	−580(8)	102(5)
P(2)	2 796(2)	3 710(2)	846(2)	
C(21)	1 901(3)	3 856(3)	519(4)	49(3)
C(22)	1 381(3)	4 114(3)	957(4)	63(4)
C(23)	716(3)	4 235(3)	661(4)	84(4)
C(24)	569(3)	4 096(3)	−74(4)	83(4)
C(25)	1 089(3)	3 838(3)	−512(4)	83(4)
C(26)	1 755(3)	3 717(3)	−215(4)	68(4)
C(27)	2 854(8)	4 036(6)	1 764(7)	89(5)
C(28)	3 277(8)	4 249(6)	328(8)	93(5)
P(3)	2 047(2)	2 391(2)	1 564(2)	
C(31)	2 097(4)	1 659(3)	1 948(4)	56(3)
C(32)	1 662(4)	1 213(3)	1 689(4)	68(4)
C(33)	1 717(4)	657(3)	1 989(4)	90(5)
C(34)	2 207(4)	546(3)	2 548(4)	86(4)
C(35)	2 642(4)	991(3)	2 807(4)	90(5)
C(36)	2 587(4)	1 548(3)	2 507(4)	74(4)
C(37)	1 231(6)	2 402(6)	1 057(7)	69(4)
C(38)	1 845(7)	2 805(6)	2 392(7)	85(4)
C*(1)	3 964(11)	959(9)	−1 744(11)	138(7)
C*(2)	3 925(9)	383(8)	−1 720(10)	119(6)
C*(3)	4 453(10)	52(8)	−2 112(10)	125(6)
C*(4)[b]	5 000	356(11)	−2 500	109(8)
C*(5)[b]	5 000	934(11)	−2 500	110(8)
C*(6)	4 454(9)	1 223(7)	−2 104(9)	108(5)
O*(7)[c]	4 753(11)	1 872(9)	−2 217(11)	125(8)
H(2)	3 876	1 466	1 492	58(30)
H(3)	3 831	423	1 152	129(49)
H(4)	3 087	117	119	71(32)
H(5)	2 160	396	−886	60(30)
H(6)	1 563	1 165	−1 524	115(46)
H(7)	1 733	2 194	−1 216	50(28)
H(12)	3 940	3 207	−1 290	199(31)
H(13)	4 290	4 108	−1 939	199(31)
H(14)	5 114	4 800	−1 341	199(31)
H(15)	5 587	4 590	−94	199(31)
H(16)	5 236	3 688	554	199(31)
H(17A)	4 948	2 174	1 065	94(9)
H(17B)	5 115	2 928	1 096	94(9)
H(17C)	5 418	2 512	341	94(9)
H(18A)	3 884	2 249	−962	94(9)
H(18B)	4 293	1 772	−330	94(9)
H(18C)	4 814	2 244	−872	94(9)
H(22)	1 495	4 221	1 526	130(21)
H(23)	314	4 435	1 000	130(21)
H(24)	54	4 189	−303	130(21)
H(25)	976	3 731	−1 080	130(21)
H(26)	2 157	3 517	−555	130(21)
H(27A)	2 550	3 846	2 207	94(9)
H(27B)	2 662	4 469	1 652	94(9)
H(27C)	3 405	4 056	1 923	94(9)
H(28A)	3 290	4 145	−254	94(9)
H(28B)	3 796	4 183	564	94(9)
H(28C)	3 122	4 697	398	94(9)
H(32)	1 283	1 299	1 256	180(28)
H(33)	1 380	312	1 788	180(28)
H(34)	2 249	115	2 780	180(28)
H(35)	3 021	905	3 240	180(28)
H(36)	2 924	1 893	2 707	180(28)
H(37A)	1 251	2 106	594	94(9)
H(37B)	1 121	2 835	860	94(9)
H(37C)	817	2 267	1 432	94(9)
H(38A)	1 659	3 234	2 249	94(9)
H(38B)	2 276	2 840	2 781	94(8)
H(38C)	1 418	2 559	2 636	94(9)

(*b*) Anisotropic thermal parameters, U_{ij} (10^4 Å^2), from the expression $\exp[-2\pi^2 . 10^{-4}(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$

Atom	U_{11}	U_{22}	U_{33}
W	350(3)	487(4)	562(4)
I(1)	758(10)	769(10)	1 122(12)
I(2)	709(10)	1 005(11)	707(10)
N(2)	406(61)	649(70)	480(69)
N(3)	746(91)	747(104)	714(95)
P(1)	462(22)	564(23)	699(24)
P(2)	451(23)	544(24)	938(29)
P(3)	357(20)	654(23)	557(22)

Atom	U_{12}	U_{13}	U_{23}
W	7(3)	−22(3)	−53(3)
I(1)	0	−97(9)	0
I(2)	0	−208(8)	0
N(2)	28(54)	−61(57)	−146(58)
N(3)	−75(95)	−79(75)	−176(116)
P(1)	12(18)	83(19)	−30(20)
P(2)	37(18)	46(21)	−34(22)
P(3)	10(18)	−17(17)	−69(19)

[a] Asterisked atoms are those of the solvent molecule. [b] This atom lies on a crystallographic two-fold symmetry axis. [c] This atom has a site occupancy factor of 0.5.

TABLE 4

Atomic parameters for (2). E.s.d.s are given in parentheses

(*a*) Co-ordinates (fractional $\times 10^4$) and isotropic thermal parameters, $U_{iso.}$ (10^3 Å^2)

Atom	x	y	z	$U_{iso.}$
Mo	7 600.3(3)	4 758.4(4)	2 791.1(3)	
I	8 829.8(3)	5 285.3(5)	6 139.9(3)	
N(1)	8 081(3)	5 418(3)	1 836(2)	32(1)
C(2)	8 810(4)	5 963(5)	1 868(3)	43(1)
C(3)	8 995(4)	6 426(5)	1 216(3)	49(2)
C(4)	8 440(4)	6 314(5)	513(4)	50(2)
C(4A)	7 673(4)	5 715(4)	440(3)	38(1)
C(5)	7 051(4)	5 545(5)	−259(4)	50(2)
C(6)	6 321(4)	4 990(5)	−253(4)	50(2)
C(7)	6 153(4)	4 582(4)	429(3)	40(1)
C(8)	6 743(3)	4 726(4)	1 122(3)	31(1)
C(8A)	7 514(3)	5 298(4)	1 124(3)	31(1)
O(8)	6 636(2)	4 385(3)	1 798(2)	34(1)
N(2)	8 431(3)	5 138(4)	3 571(3)	
N(3)	9 059(4)	5 558(6)	4 131(4)	
H(3A)	9 012(46)	5 485(58)	4 656(43)	86(20)
H(3B)	9 464(51)	5 463(70)	4 044(50)	86(20)
P(1)	6 912(1)	6 484(1)	2 828(1)	

TABLE 4 (*continued*)

Atom	x	y	z	$U_{\text{iso.}}$
C(11)	6 399(4)	6 792(4)	3 622(3)	36(1)
C(12)	6 887(4)	6 704(5)	4 376(3)	49(2)
C(13)	6 516(4)	6 936(5)	4 988(4)	60(2)
C(14)	5 662(4)	7 250(5)	4 853(4)	60(2)
C(15)	5 169(4)	7 329(5)	4 114(4)	56(2)
C(16)	5 538(4)	7 112(5)	3 498(4)	48(2)
C(17)	7 714(4)	7 512(5)	2 915(4)	60(2)
C(18)	6 108(4)	6 835(5)	1 959(3)	52(2)
P(2)	6 628(1)	3 873(1)	3 521(1)	
C(21)	5 496(3)	4 343(4)	3 350(3)	34(1)
C(22)	5 080(4)	4 538(5)	3 939(4)	48(2)
C(23)	4 209(4)	4 834(5)	3 776(4)	54(2)
C(24)	3 749(4)	4 942(5)	3 032(3)	48(2)
C(25)	4 159(4)	4 756(5)	2 442(4)	49(2)
C(26)	5 024(4)	4 459(4)	2 595(3)	41(1)
C(27)	6 425(4)	2 509(5)	3 339(4)	57(2)
C(28)	7 024(4)	3 887(5)	4 563(3)	53(2)
P(3)	8 327(1)	3 109(1)	2 531(1)	
C(31)	8 664(4)	2 225(5)	3 347(3)	45(2)
C(32)	8 638(5)	1 160(6)	3 258(4)	64(2)
C(33)	8 874(5)	552(7)	3 922(5)	82(2)
C(34)	9 124(5)	964(7)	4 624(5)	80(2)
C(35)	9 187(5)	2 002(6)	4 728(5)	72(2)
C(36)	8 945(4)	2 634(5)	4 076(4)	56(2)
C(37)	7 679(4)	2 356(5)	1 749(4)	62(2)
C(38)	9 329(4)	3 263(6)	2 199(4)	62(2)
H(2)	9 220	6 038	2 357	83
H(3)	9 517	6 826	1 266	83
H(4)	8 567	6 638	67	83
H(5)	7 143	5 819	−735	83
H(6)	5 905	4 872	−733	83
H(7)	5 625	4 204	412	83
H(12)	7 484	6 482	4 473	76
H(13)	6 857	6 878	5 509	76
H(14)	5 410	7 414	5 281	76
H(15)	4 568	7 534	4 024	76
H(16)	5 195	7 185	2 979	76
H(17A)	8 035	7 435	2 520	66
H(17B)	8 109	7 479	3 414	66
H(17C)	7 420	8 164	2 855	66
H(18A)	5 649	6 333	1 859	66
H(18B)	6 381	6 859	1 529	66
H(18C)	5 870	7 497	2 029	66
H(22)	5 397	4 469	4 467	82
H(23)	3 929	4 963	4 193	82
H(24)	3 147	5 146	2 921	82
H(25)	3 838	4 832	1 915	82
H(26)	5 299	4 334	2 175	82
H(27A)	6 972	2 152	3 407	66
H(27B)	6 092	2 412	2 818	66
H(27C)	6 105	2 241	3 694	66
H(28A)	7 157	4 580	4 736	66
H(28B)	7 541	3 473	4 705	66
H(28C)	6 583	3 615	4 801	66
H(32)	8 463	853	2 755	97
H(33)	8 854	−183	3 870	97
H(34)	9 264	520	5 067	97
H(35)	9 391	2 291	5 234	97
H(36)	8 975	3 367	4 138	97
H(37A)	7 119	2 217	1 854	66
H(37B)	7 972	1 720	1 705	66
H(37C)	7 603	2 733	1 274	66
H(38A)	9 740	3 659	2 570	66
H(38B)	9 204	3 613	1 710	66
H(38C)	9 573	2 600	2 141	66

(*b*) Anisotropic thermal parameters, U_{ij} (10^4 Å^2), from the expression $\exp[-2\pi^2 . 10^{-4}(U_{11}h^2a^{*2} + . . . + 2U_{12}hka^*b^* + . . .)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	263(2)	328(3)	300(3)	8(2)	36(2)	12(2)
I	625(3)	1 014(4)	661(3)	−245(3)	24(2)	54(3)
N(2)	335(26)	408(28)	344(25)	32(22)	14(21)	15(22)
N(3)	489(38)	728(46)	554(37)	−85(34)	−98(35)	−90(34)
P(1)	394(8)	315(8)	389(8)	40(7)	96(7)	22(7)
P(2)	299(8)	358(9)	349(8)	−18(6)	41(6)	21(7)
P(3)	270(9)	376(9)	459(9)	75(7)	56(7)	−13(7)

lengths) and 7 (angles). In each complex, the three phosphine ligands are meridionally arranged, and the quinolin-8-olato-oxygen atom is *trans* to the hydrazido-(2−)-group.

As in previously reported hydrazido(2−)-structures,[1-3] the M–N–N system is essentially linear and is one of

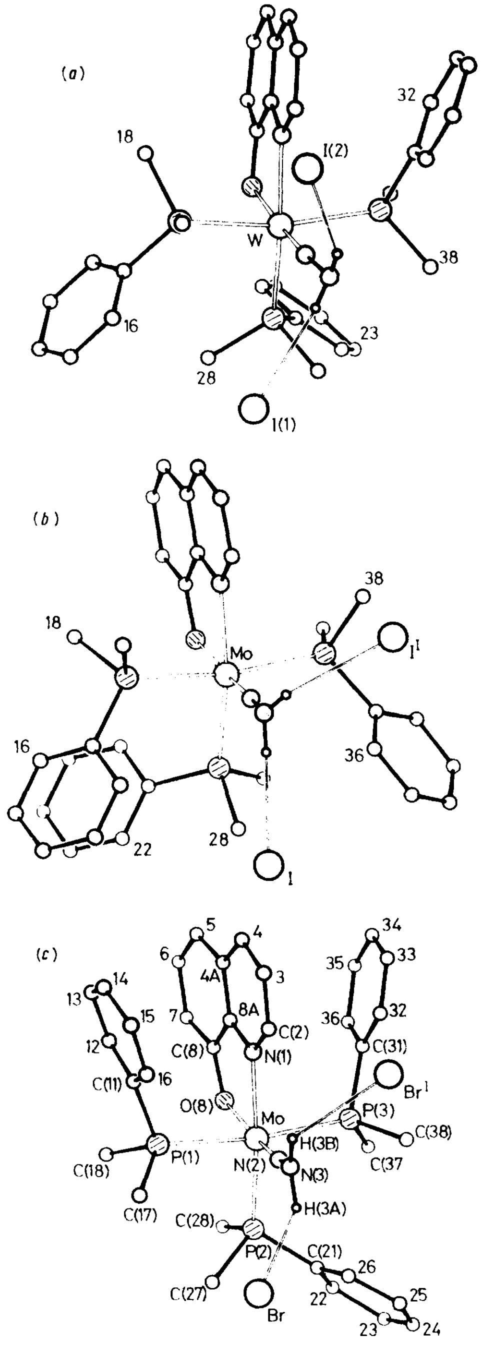


FIGURE 1 Views of the cationic complexes [(*a*) (1), (*b*) (2), (*c*) (3)] and the anions to which they are hydrogen bonded. The orientations of the cations are the same for each complex [based on the N(1)–P(2) and N(2)–O(8) vectors]. The atomic numbering scheme for (3) is common to the three complexes and only occasional identifying numbers of carbon atoms are shown for (1) and (2). Symmetry codes, Roman numeral superscripts, are identified in the legends to Figures 2—4

considerable multiple bonding with delocalisation of electrons throughout its length. The dimensions in our three structures are very similar and compare well with those in Table 5 of ref. 3; molybdenum and tungsten have essentially identical crystal radii and their complexes may be compared directly. The position of N(3) with respect to pairs of anions indicated good hydrogen-bonding arrangements in each structure; the location of some, and the refinement of all of the hydrazido-hydrogen atoms, approximately on lines between N(3) and the anions confirmed the hydrogen bonding (Table 8). Similar strong hydrogen-bonding interactions have been noted for other hydrazido(2−)-hydrogen atoms, *e.g.* in $[WCl_3(NNHR)(PMe_2Ph)_2]$, R = H and Ph,[10] $[WBr(NNH_2)(PMe_2Ph)_3(MeC_5H_4N)]Br$,[1] and $[WClBr(NNH_2)H(PMe_2Ph)_3]Br$.[2]

TABLE 5

Atomic parameters for (3). E.s.d.s are given in parentheses

(*a*) Co-ordinates (fractional $\times 10^4$) and isotropic thermal parameters, $U_{iso.}$ (10^3 Å^2)

Atom	*x*	*y*	*z*	$U_{iso.}$
Mo	0	6 105.3(2)	5 000	
Br	297(2)	4 505.5(4)	4 059(2)	
N(1)	−1 762(8)	6 471(2)	3 786(8)	37(2)
C(2)	−3 029(11)	6 334(3)	3 055(11)	45(3)
C(3)	−4 055(13)	6 602(4)	2 319(13)	58(3)
C(4)	−3 826(13)	7 005(4)	2 274(13)	60(3)
C(4A)	−2 490(11)	7 162(3)	2 994(11)	48(3)
C(5)	−2 065(15)	7 564(4)	2 992(14)	74(4)
C(6)	−727(14)	7 668(4)	3 697(13)	68(4)
C(7)	235(13)	7 384(4)	4 445(12)	59(3)
C(8)	−115(10)	6 989(3)	4 524(10)	43(2)
C(8A)	−1 478(11)	6 873(3)	3 754(11)	46(3)
O(8)	729(7)	6 706(2)	5 263(7)	47(2)
N(2)	−826(8)	5 641(3)	4 531(8)	40(2)
N(3)	−1 613(13)	5 322(4)	3 936(11)	62(3)
H(3A)	−1 056(104)	5 062(34)	4 347(102)	49(30)
H(3B)	−2 507(256)	5 343(58)	3 295(207)	202(85)
P(1)	661(3)	6 089(1)	3 069(3)	44(1)
C(11)	−680(12)	6 302(4)	1 566(11)	48(3)
C(12)	−684(12)	6 702(4)	1 255(12)	56(3)
C(13)	−1 740(16)	6 851(5)	88(15)	82(4)
C(14)	−2 765(17)	6 596(5)	−628(16)	81(4)
C(15)	−2 802(19)	6 215(5)	−276(17)	96(5)
C(16)	−1 732(15)	6 056(5)	855(15)	77(4)
C(17)	945(16)	5 595(5)	2 478(15)	79(4)
C(18)	2 149(14)	6 380(4)	3 219(14)	74(4)
P(2)	2 236(3)	5 835(1)	6 515(3)	48(1)
C(21)	2 378(13)	5 562(4)	7 999(12)	55(3)
C(22)	3 319(16)	5 679(5)	9 229(15)	82(4)
C(23)	3 336(20)	5 433(6)	10 340(19)	101(5)
C(24)	2 481(21)	5 138(6)	10 142(20)	113(6)
C(25)	1 502(21)	5 024(6)	8 932(20)	118(6)
C(26)	1 531(16)	5 249(5)	7 857(16)	83(4)
C(27)	3 056(16)	5 453(5)	5 860(15)	78(4)
C(28)	3 519(17)	6 233(5)	7 090(16)	91(5)
P(3)	−713(3)	6 244(1)	6 864(3)	46(1)
C(31)	−1 922(11)	6 667(4)	6 531(11)	51(3)
C(32)	−1 456(14)	7 056(4)	6 850(13)	69(4)
C(33)	−2 367(19)	7 388(6)	6 551(18)	96(5)
C(34)	−3 680(20)	7 322(6)	5 880(18)	103(5)
C(35)	−4 212(18)	6 922(5)	5 521(16)	88(4)
C(36)	−3 320(13)	6 597(4)	5 804(13)	61(3)
C(37)	567(16)	6 388(5)	8 459(15)	84(5)
C(38)	−1 600(14)	5 819(4)	7 235(14)	73(4)
H(2)	−3 248	6 013	3 041	55
H(3)	−5 066	6 485	1 768	68
H(4)	−4 644	7 206	1 697	71
H(5)	−2 788	7 793	2 437	84
H(6)	−411	7 978	3 672	78
H(7)	1 280	7 479	4 971	68
H(12)	99	6 904	1 885	67
H(13)	−1 727	7 162	−222	92
H(14)	−3 572	6 709	−1 509	91
H(15)	−3 647	6 022	−853	106
H(16)	−1 758	5 744	1 145	87
H(17A)	1 720	5 432	3 268	90
H(17B)	1 273	5 638	1 686	90
H(17C)	8	5 422	2 130	90
H(18A)	2 077	6 682	3 569	84
H(18B)	2 208	6 401	2 273	84
H(18C)	3 052	6 232	3 906	84
H(22)	3 991	5 935	9 360	93
H(23)	4 067	5 498	11 322	112
H(24)	2 533	4 966	10 987	122
H(25)	779	4 784	8 821	128
H(26)	835	5 165	6 879	93
H(27A)	3 071	5 562	4 949	88
H(27B)	2 490	5 172	5 686	88
H(27C)	4 088	5 401	6 559	88
H(28A)	3 147	6 478	7 503	101
H(28B)	3 729	6 346	6 278	101
H(28C)	4 442	6 111	7 831	101
H(32)	−373	7 111	7 334	78
H(33)	−1 997	7 691	6 875	106
H(34)	−4 368	7 578	5 589	113
H(35)	−5 297	6 874	5 032	98
H(36)	−3 691	6 294	5 475	71
H(37A)	1 361	6 161	8 783	93
H(37B)	101	6 410	9 157	93
H(37C)	1 000	6 679	8 382	93
H(38A)	−2 394	5 710	6 338	83
H(38B)	−2 047	5 919	7 900	83
H(38C)	−885	5 576	7 684	83

(*b*) Anisotropic thermal parameters, U_{ij} (10^4 Å^2), from the expression $\exp[-2\pi^2 . 10^{-4}(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	313(4)	342(4)	358(4)	28(4)	131(3)	10(5)
Br	478(6)	640(7)	862(9)	72(7)	335(6)	−45(7)

Each of the NH_2 groups lies roughly in the plane of the quinolin-8-olato-ligand and P(2). The conformation at N(3), whether considering bonding of N(3) to its hydrogen atoms or to the more precisely located anions, is not planar; the shallow tetrahedron formed by N(2), N(3), and either the hydrogen atoms or the anions is most

TABLE 6

Bond lengths (Å)

	Complex		
	(1)	(2)	(3)
(*a*) About the metal ion			
M–N(1)	2.188(8)	2.189(4)	2.189(7)
M–O(8)	2.097(7)	2.102(3)	2.101(7)
M–P(1)	2.517(3)	2.500(2)	2.515(4)
M–P(2)	2.475(3)	2.504(2)	2.476(3)
M–P(3)	2.488(3)	2.526(2)	2.519(4)
M–N(2)	1.753(10)	1.743(4)	1.735(8)
(*b*) In quinolin-8-olate ligand			
N(1)–C(2)	1.327(12)	1.339(7)	1.349(12)
N(1)–C(8A)	1.389(12)	1.379(6)	1.358(13)
C(2)–C(3)	1.411(14)	1.394(8)	1.391(15)
C(3)–C(4)	1.362(15)	1.357(8)	1.352(18)
C(4)–C(4A)	1.392(14)	1.418(8)	1.428(16)
C(4A)–C(5)	1.424(15)	1.409(8)	1.397(18)
C(4A)–C(8A)	1.408(14)	1.405(7)	1.437(14)
C(5)–C(6)	1.344(15)	1.361(8)	1.372(19)
C(6)–C(7)	1.391(15)	1.403(8)	1.392(17)
C(7)–C(8)	1.394(14)	1.374(7)	1.364(16)
C(8)–C(8A)	1.389(14)	1.424(7)	1.417(14)
C(8)–O(8)	1.331(12)	1.327(6)	1.328(11)

TABLE 6 (*continued*)

(*c*) In phosphine ligands

P(1)–C(11)	1.792(8)	1.826(5)	1.850(10)
P(1)–C(17)	1.805(13)	1.822(7)	1.824(16)
P(1)–C(18)	1.829(14)	1.814(6)	1.808(16)
C(11)–C(12)	1.395	1.387(8)	1.36(2)
C(11)–C(16)	1.395	1.386(8)	1.35(2)
C(12)–C(13)	1.395	1.382(9)	1.43(2)
C(13)–C(14)	1.395	1.372(9)	1.36(2)
C(14)–C(15)	1.395	1.366(9)	1.32(2)
C(15)–C(16)	1.395	1.383(8)	1.42(2)
P(2)–C(21)	1.823(7)	1.843(5)	1.831(14)
P(2)–C(27)	1.826(13)	1.820(7)	1.842(18)
P(2)–C(28)	1.801(13)	1.813(6)	1.817(16)
C(21)–C(22)	1.395	1.380(8)	1.39(2)
C(21)–C(26)	1.395	1.385(7)	1.34(2)
C(22)–C(23)	1.395	1.390(8)	1.47(3)
C(23)–C(24)	1.395	1.360(8)	1.29(3)
C(24)–C(25)	1.395	1.375(8)	1.39(3)
C(25)–C(26)	1.395	1.381(8)	1.42(3)
P(3)–C(31)	1.825(7)	1.831(6)	1.834(12)
P(3)–C(37)	1.795(12)	1.810(6)	1.818(14)
P(3)–C(38)	1.816(13)	1.818(6)	1.826(16)
C(31)–C(32)	1.395	1.394(9)	1.37(2)
C(31)–C(36)	1.395	1.375(8)	1.41(2)
C(32)–C(33)	1.395	1.398(10)	1.41(2)
C(33)–C(34)	1.395	1.331(10)	1.32(3)
C(34)–C(35)	1.395	1.363(10)	1.42(3)
C(35)–C(36)	1.395	1.401(9)	1.38(2)

(*d*) In hydrazido-ligand

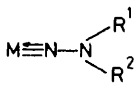
N(2)–N(3)	1.360(17)	1.347(7)	1.344(14)
N(3)–H(3A)	0.81(9)	0.96(7)	1.04(11)
N(3)–H(3B)	0.69(11)	0.70(8)	0.94(21)

(*e*) In solvent molecule [complex (1) structure only]

C*(1)–C*(2)	1.33(2)	C*(4)–C*(5)	1.33(3)
C*(1)–C*(6)	1.29(2)	C*(5)–C*(6)	1.42(2)
C*(2)–C*(3)	1.44(2)	C*(6)–O*(7)	1.61(2)
C*(3)–C*(4)	1.43(2)	O*(7) · · · O*(7′)	1.39(4)

Primed solvent atoms have co-ordinates $1 - x, y, -\frac{1}{2} - z$.

pronounced in (1) [Figures 1(*a*) and 2]. (Further details of planes through various groups of atoms are in Table 9 which has been deposited in SUP 22889.) This non-planarity about N(3) and the dimensions of the M–N–N system indicate that in our three complexes the bonding



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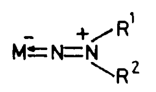

B

TABLE 7

Bond angles (°)

	Complex		
	(1)	(2)	(3)
(*a*) About metal ion			
N(1)–M–O(8)	74.9(3)	75.6(1)	75.5(3)
N(1)–M–P(1)	84.8(2)	84.2(1)	87.2(3)
N(1)–M–P(2)	163.3(2)	160.9(1)	167.7(2)
N(1)–M–P(3)	84.2(2)	86.5(1)	86.5(3)
N(1)–M–N(2)	102.4(4)	100.1(2)	95.0(3)
O(8)–M–P(1)	89.2(2)	89.8(1)	85.6(3)
O(8)–M–P(2)	88.7(2)	85.3(1)	92.2(2)
O(8)–M–P(3)	88.4(2)	85.4(1)	86.2(3)
O(8)–M–N(2)	177.0(4)	175.6(2)	169.9(3)
P(1)–M–P(2)	97.9(1)	94.5(1)	92.8(1)
P(1)–M–P(3)	169.1(1)	170.3(1)	170.7(1)
P(1)–M–N(2)	91.7(3)	88.6(2)	90.5(4)
P(2)–M–P(3)	92.7(1)	93.5(1)	91.9(1)
P(2)–M–N(2)	94.0(3)	98.9(2)	97.3(3)
P(3)–M–N(2)	90.2(3)	95.6(2)	97.0(4)

TABLE 7 (*continued*)

(*b*) In quinolin-8-olate ligand

M–N(1)–C(2)	128.6(7)	128.5(4)	126.8(7)
M–N(1)–C(8A)	113.4(7)	113.6(3)	113.8(6)
C(8A)–N(1)–C(2)	117.8(9)	117.8(5)	119.4(8)
N(1)–C(2)–C(3)	123.0(11)	122.4(5)	120.6(10)
C(2)–C(3)–C(4)	118.5(12)	120.3(6)	122.1(11)
C(3)–C(4)–C(4A)	121.2(12)	119.8(6)	119.3(11)
C(4)–C(4A)–C(5)	125.5(11)	124.8(5)	126.5(10)
C(4)–C(4A)–C(8A)	117.2(11)	116.8(5)	116.2(10)
C(5)–C(4A)–C(8A)	117.2(11)	118.3(5)	117.3(10)
C(4A)–C(5)–C(6)	119.2(13)	119.5(6)	120.0(12)
C(5)–C(6)–C(7)	124.0(13)	122.4(6)	121.9(13)
C(6)–C(7)–C(8)	118.2(12)	120.0(5)	121.3(11)
C(7)–C(8)–C(8A)	119.1(11)	118.2(5)	117.5(9)
C(7)–C(8)–O(8)	123.4(11)	124.4(5)	124.8(9)
C(8A)–C(8)–O(8)	117.5(10)	117.4(4)	117.8(9)
C(8)–C(8A)–N(1)	115.6(10)	115.6(4)	115.8(9)
C(8)–C(8A)–C(4A)	122.2(10)	121.5(5)	121.8(10)
N(1)–C(8A)–C(4A)	122.1(10)	122.9(5)	122.4(9)
M–O(8)–C(8)	117.6(7)	117.6(3)	116.7(6)

(*c*) In phosphine ligands

M–P(1)–C(11)	125.4(3)	119.3(2)	112.5(5)
M–P(1)–C(17)	108.4(5)	111.4(2)	118.0(6)
M–P(1)–C(18)	112.1(5)	115.2(2)	116.6(5)
C(11)–P(1)–C(17)	103.5(6)	101.2(3)	101.1(6)
C(11)–P(1)–C(18)	102.3(6)	104.9(3)	102.7(6)
C(17)–P(1)–C(18)	102.6(7)	102.7(3)	103.8(8)
P(1)–C(11)–C(12)	118.6(3)	118.9(4)	121.2(8)
P(1)–C(11)–C(16)	121.3(3)	122.3(4)	117.8(10)
C(16)–C(11)–C(12)	120	118.8(5)	120.7(10)
C(11)–C(12)–C(13)	120	120.1(6)	119.1(11)
C(12)–C(13)–C(14)	120	120.2(7)	118.8(14)
C(13)–C(14)–C(15)	120	120.4(7)	121.7(14)
C(14)–C(15)–C(16)	120	119.8(6)	120.2(15)
C(15)–C(16)–C(11)	120	120.7(6)	119.1(14)
M–P(2)–C(21)	115.3(3)	116.5(2)	119.9(4)
M–P(2)–C(27)	111.0(5)	117.4(2)	117.4(4)
M–P(2)–C(28)	123.1(5)	114.7(2)	111.8(5)
C(21)–P(2)–C(27)	106.0(6)	99.8(3)	98.0(7)
C(21)–P(2)–C(28)	99.9(6)	104.8(3)	104.9(7)
C(27)–P(2)–C(28)	99.2(7)	101.3(3)	102.6(8)
P(2)–C(21)–C(22)	123.1(3)	123.2(4)	121.2(11)
P(2)–C(21)–C(26)	116.8(3)	118.5(4)	117.5(10)
C(26)–C(21)–C(22)	120	118.2(5)	121.2(14)
C(21)–C(22)–C(23)	120	120.8(6)	115.9(14)
C(22)–C(23)–C(24)	120	120.6(6)	119.9(16)
C(23)–C(24)–C(25)	120	119.1(6)	125.4(22)
C(24)–C(25)–C(26)	120	121.0(6)	114.6(19)
C(25)–C(26)–C(21)	120	120.3(5)	122.9(14)
M–P(3)–C(31)	112.8(3)	116.7(2)	113.1(4)
M–P(3)–C(37)	116.9(4)	113.7(2)	119.4(7)
M–P(3)–C(38)	116.7(5)	115.4(2)	113.7(5)
C(31)–P(3)–C(37)	104.5(5)	106.1(3)	101.3(6)
C(31)–P(3)–C(38)	100.4(5)	102.3(3)	103.7(6)
C(37)–P(3)–C(38)	103.5(6)	100.9(3)	103.7(7)
P(3)–C(31)–C(32)	121.3(3)	122.6(5)	120.2(9)
P(3)–C(31)–C(36)	118.7(3)	118.3(5)	119.7(9)
C(36)–C(31)–C(32)	120	119.1(6)	119.7(11)
C(31)–C(32)–C(33)	120	118.1(7)	121.0(13)
C(32)–C(33)–C(34)	120	121.8(8)	119.1(17)
C(33)–C(34)–C(35)	120	121.5(9)	121.8(18)
C(34)–C(35)–C(36)	120	118.2(8)	119.2(15)
C(35)–C(36)–C(31)	120	121.2(7)	118.9(12)

(*d*) In hydrazido-ligand

M–N(2)–N(3)	174.7(9)	172.3(5)	168.3(8)
N(2)–N(3)–H(3A)	106(9)	118(5)	107(5)
N(2)–N(3)–H(3B)	106(13)	108(8)	124(12)
H(3A)–N(3)–H(3B)	139(15)	118(9)	129(13)

(*e*) In solvent molecule [structure of complex (1) only]

C*(6)–C*(1)–C*(2)	122(2)	C*(6)–C*(5)–C*(6′)	124(1)
C*(1)–C*(2)–C*(3)	118(2)	C*(5)–C*(6)–C*(1)	124(2)
C*(2)–C*(3)–C*(4)	119(2)	C*(5)–C*(6)–O*(7)	97(2)
C*(3)–C*(4)–C*(5)	119(1)	C*(1)–C*(6)–O*(7)	139(2)
C*(3)–C*(4)–C*(3′)	122(1)	C*(6)–O*(7)–O*(7′)	109(2)
C*(4)–C*(5)–C*(6)	118(1)		

pattern is of form A rather than B; the form B has been proposed as predominant in the oxo-complex [Mo(NNMe$_2$)O(S$_2$CNMe$_2$)$_2$] [11] and in the [ReCl$_2$(NH$_3$)(NNHPh)(PMe$_2$Ph)$_2$]$^+$ cation,[12] whereas A is favoured in most other hydrazido(2—)-complexes.

In the quinolin-8-olato-ligands, the variation in bond dimensions (Tables 6 and 7) in the aromatic systems in each structure follows the normal trends.[13,14] None of the ligands is strictly planar; all are curved to accommodate neighbouring groups. The metal ions are not far removed [0.10 Å in (2) to 0.26 Å in (1)] from the mean planes of the quinolin-8-olato-ligands. The chelation of the metal ions by N(1) and O(8) in each complex shows the M–N distance *ca.* 0.09 Å longer than the M–O bond; this value corresponds well with that of 0.13 Å in the tungsten(IV) complex W(QBr)$_4$·C$_6$H$_6$ (where QBr is the 5-bromoquinolin-8-olato-ion), in which the co-ordination is eight-fold, dodecahedral.[13] The actual co-ordination distances in this complex are very similar to ours; the expected shortening of bonds in going from eight- to six-co-ordination appears balanced by a combination of (i) the π-bonding effects of the hydrazido-ligand and (ii) the steric effects of the neighbouring bulky phosphine ligands and the close-in hydrazido-ligand; angles subtended at the metal atom (Table 7 and Figure 1) suggest a squeezing out of the quinolin-8-olato-ligand. In the molybdenum(VI) complex [MoO$_2$(quin)$_2$],[15] Mo–N and Mo–O(quin) are 2.32 and 1.98 Å with the N atoms *trans* to the oxido-atoms; not only is the metal in a high oxidation, d^0, state, encouraging shorter M–O and longer M–N bonds (from π donation by the phenolato-oxygen atoms, and lack of π donation by Mo to the nitrogen atoms), but also the *trans* influence of the π-donating oxido-atoms effectively loosens the M–N bonds. The same trends are found in the molybdenum(V) complex [(quin)OMo(μ-O)(μ-SCH$_2$CH$_2$O)MoO(quin)] where Mo–N and Mo–O are *ca.* 2.205 and 2.030 Å.[16]

There is considerable variation in the M–P bond lengths in our three structures, and little apparent system in the variation. All the lengths are significantly less than the W^{IV}–P distance of 2.550 Å reported for [WCl$_4$(PMe$_2$Ph)$_2$] [17] but this may be explained by the sharing of donated π electrons from the hydrazido- and phenolato-groups into the phosphorus empty d orbitals. The three phosphine groups are similarly arranged, in the equatorial plane, with respect to the π-donating groups, so it seems that steric effects control the variation in our M–P lengths. In [MoCl$_2$O(PEt$_2$Ph)$_3$] [18] and [MoCl$_2$O(PMe$_2$Ph)$_3$],[19] which are also *mer* triphosphine complexes of Mo^{IV}, the π-donating oxo-group (with *trans* chloro-group) seems to have little effect on the Mo–P lengths; here, the distances to the mutually *trans* phosphorus atoms are 2.541 and 2.558 Å in the first, and 2.580 and 2.553 Å in the second of these complexes.

The most obvious differences in the three cationic complexes are in the orientations of the phosphine groups. Such cations have been described as 'distortional isomers' (assuming the Mo and W atoms equivalent).[19] In (3), two phosphine phenyl groups are aligned as closely as possible with the quinolin-8-olato-ligand; in (1), one phenyl ring lies roughly parallel with that ligand; in (2), there is no such alignment, but the phenyl groups of P(1) and P(2) lie parallel. In (1), the phenyl groups were refined as rigid groups; in the other complexes the dimensions of the phosphine groups, allowing for the errors quoted, do not differ greatly from expected values, and the phenyl rings are not distorted far from planarity. In some cases the phosphorus atom is removed slightly from the ring mean plane [maximum of 0.10 Å for P(2) in (2)], in attempting to accommodate neighbouring groups.

TABLE 8

Dimensions of the hydrogen-bonding schemes.* The anionic acceptor is denoted A

	N–H	H···A	N···A	N–H···A	N–N···A	H–N–H	A···N···A'	N···A···N'
		Å				°		
(*a*) Complex (1)								
N(3)–H(3A)···I(1)	0.81	2.92	3.716	167	109.3	139	110.6	68.2
N(3)–H(3B)···I(2)	0.69	2.99	3.604	151	103.8			70.7
(*b*) Complex (2)								
N(3)–H(3A)···I	0.96	2.73	3.689	178	117.2	118	113.3	66.7
N(3)–H(3B)···I^{I}	0.70	2.95	3.637	169	108.5			
(*c*) Complex (3)								
N(3)–H(3A)···Br	1.04	2.43	3.342	146	110.8	129	136.0	116.8
N(3)–H(3B)···Br^{I}	0.94	2.84	3.411	120	106.1			

* Roman superscripts denote the symmetry operations defined in Figures 3 and 4.

In comparison with *fac*-triphosphine complexes and with complexes having four or more phosphine ligands, our cationic groups are not very sterically congested. The distortional isomerism indicates that a variety of phosphine group orientations are feasible. Nevertheless, examination shows that, in common with more crowded molecules,[20] in addition to the parallel alignments mentioned above: (i) P–M–P angles are 92—98° (*cis*) and *ca.* 170° (*trans*), (ii) groups of C–P–C atoms lie in paired parallel planes; the C atoms may be of methyl or phenyl groups, (iii) there are very short C···C interactions between neighbouring phosphine groups, *e.g.* C(Me)···C(Me) in the range 3.5—3.7 Å and C(Me)···C(Ph) down to 3.35 Å (Table 10, of short intramolecular distances, has been deposited in SUP 22889), (iv) there are examples of C(Me)–P–C–C torsion angles close to 0° [as in (2), for C(28)–P(2)–C(21)–C(22), *etc.*] and consequent short intraligand contacts; such conditions are found in conjunction with the close packing systems of (ii) above.

Of the pair of anions associated with each cation, one has a fairly fixed position with respect to the basic skeleton of the cation, *viz.* in (1), (2), and (3), the anions I(1), I, and Br respectively occupy similar positions in relation to the metal and its co-ordinated atoms. The second anions have similar positions in the molybdenum complexes but a rather different position in (1). This appears to leave the hydrazido-ligand of (1) more exposed to protonation from the lower right side in Figure 1(*a*), but it must be remembered that the conformations found in the crystal form are not necessarily those in solution where the reactions occur.

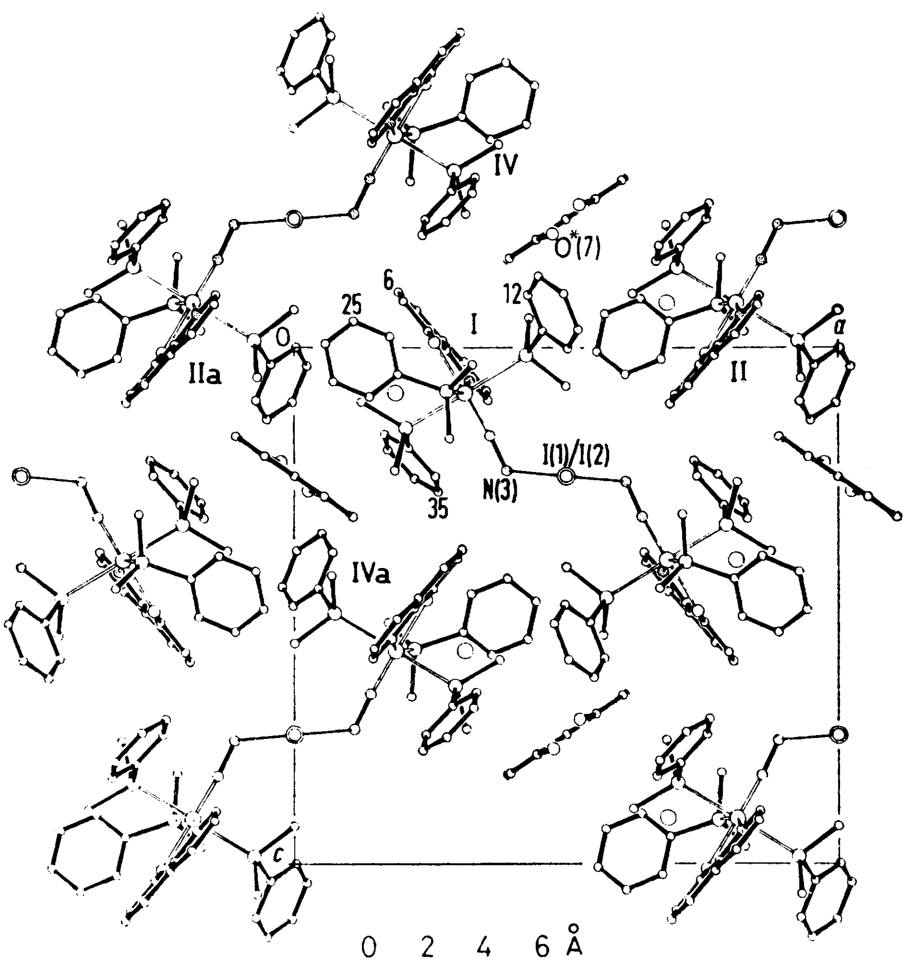

FIGURE 2 Packing arrangement for (1), viewed down the *b* axis. Only the molecules with the tungsten atom at $y \sim \frac{1}{4}$ are drawn; the positions of the metal atoms only of the other molecules are shown. In this Figure and in Figures 3 and 4, numbers of certain carbon atoms are included for identification. Symmetry codes are: I x, y, z as in Table 3; II $\frac{1}{2} + x, \frac{1}{2} - y, -z$; IIa $-\frac{1}{2} + x, \frac{1}{2} - y, -z$; IV $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$; IVa $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$

Another important feature and point of contrast in these *crystal* structures is in the extended hydrogen-bonding schemes. We have noted the similarities in hydrogen bonding of each cation to a pair of neighbouring anions. Looking further, we find that in the iodide structures, pairs of cations are linked *via* hydrogen bonds, through pairs of anions to form dimer units; in (1), a two-fold symmetry axis at ($\frac{1}{2}, y, \frac{1}{4}$) passes through the two anions, I(1) and I(2), and the two cations are related by this symmetry; in (2), a centre of symmetry at (1, $\frac{1}{2}$, $\frac{1}{2}$) relates the pairs of cations and iodide ions. However, in (3), hydrogen bonding links cations and anions in chains, along the glide planes, parallel to the *a* axis, through the crystal. These features may be discerned in the packing diagrams, Figures 2—4.

From the variations in phosphine group orientation and in the extended hydrogen-bonding schemes, we expect, and find (Figures 2—4), little similarity in the packing arrangement of the three complexes. However, good packing features are found in each structure; there

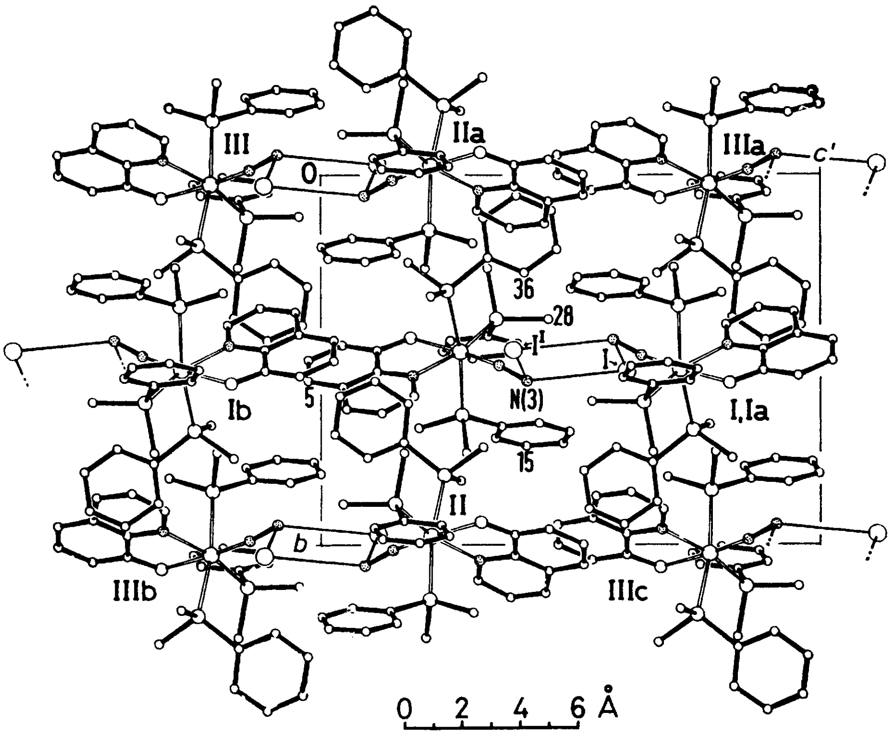

FIGURE 3 Packing arrangement for (2), viewed down the a axis. Note that 'c'' indicates 'c sin β,' in the plane normal to the a axis. Symmetry codes relating to the molecule at x, y, z in Table 4 are: I $2 - x, 1 - y, 1 - z$; Ia $1 - x, 1 - y, 1 - z$; Ib $1 - x, 1 - y, -z$; II $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; IIa $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; III $x, \frac{1}{2} - y, -\frac{1}{2} + z$; IIIa $x, \frac{1}{2} - y, \frac{1}{2} + z$; IIIb $x, \frac{3}{2} - y, -\frac{1}{2} + z$; IIIc $x, \frac{3}{2} - y, \frac{1}{2} + z$

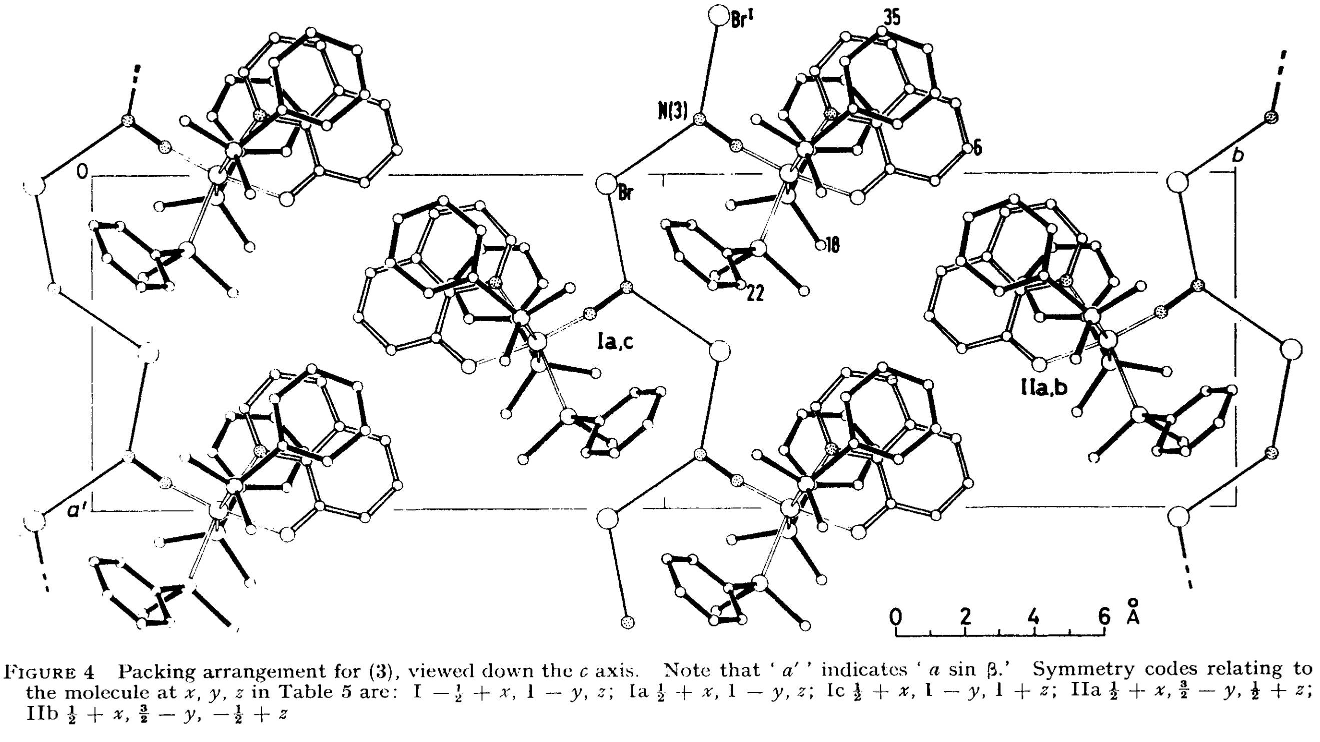

FIGURE 4 Packing arrangement for (3), viewed down the c axis. Note that 'a'' indicates 'a sin β.' Symmetry codes relating to the molecule at x, y, z in Table 5 are: I $-\frac{1}{2} + x, 1 - y, z$; Ia $\frac{1}{2} + x, 1 - y, z$; Ic $\frac{1}{2} + x, 1 - y, 1 + z$; IIa $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; IIb $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$

are, for example, several cases of hydrogen atoms directed towards the centres of neighbouring aromatic systems in each structure, *e.g.* **H(23)** in (1) is approximately equidistant (2.82—**3.02** Å) from the six atoms C*(1)—C*(6) of a quinolin-8-ol molecule, and, in (2), H(3) is similarly close to the phenyl ring C(31)–C(**36**) in an adjacent molecule. Some of the shorter intermolecular van der Waals contacts are in Tables **11**—**13** of SUP 22889.

In addition to the strong hydrogen bonds noted above, all the anions have other close neighbours whose contacts with the anions might be classed as weaker C–H · · · X hydrogen bonds. In particular, (a) in (1), C(2) · · · I(2) and H(2) · · · I(2) are **3.831** and **2.80** Å, and (b) in (3), C(2) · · · Br^{I} and H(2) · · · Br^{I} are **3.697** and 2.83 Å, and C(27) · · · Br^{Ia} is **3.689** Å.

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REFERENCES

[1] J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589.

[2] T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, and M. Hidai, *J. Amer. Chem. Soc.*, 1979, **101**, 3405.

[3] J. Chatt, A. J. Pearman, and R. L. Richards, *J.C.S. Dalton*, 1978, 1766.

[4] J. Chatt, M. E. Fakley, R. L. Richards, I. R. Hanson, and D. L. Hughes, *J. Organometallic Chem.*, 1979, **170**, C6.

[5] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.

[6] SHELX-76, Program for Crystal Structure Determination, by G. M. Sheldrick, University of Cambridge.

[7] CAD4, processor program, from M. B. Hursthouse, Queen Mary College, London.

[8] ORTEP, by C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, U.S.A.

[9] X-RAY ARC Library of Programs for the IBM 1130 Computer, *J. Appl. Cryst.*, 1973, **6**, 309.

[10] J. Chatt, M. E. Fakley, P. B. Hitchcock, R. L. Richards, N. T. Luong-Thi, and D. L. Hughes, *J. Organometallic Chem.*, 1979, **172**, C55.

[11] M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, and M. Motevalli, *J.C.S. Dalton*, 1979, 1600.

[12] R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *J. Amer. Chem. Soc.*, 1974, **96**, 260.

[13] W. D. Bonds, R. D. Archer, and W. C. Hamilton, *Inorg. Chem.*, 1971, **10**, 1764.

[14] D. L. Hughes and M. R. Truter, *J.C.S. Dalton*, 1979, 520.

[15] L. O. Atovmyan and Yu. A. Sokolova, *Chem. Comm.*, 1969, 649.

[16] J. I. Gelder, J. H. Enemark, G. Wolterman, D. A. Boston, and G. P. Haight, *J. Amer. Chem. Soc.*, 1975, **97**, 1616.

[17] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Comm.*, 1970, 30.

[18] Lj. Manojlovic-Muir, *J. Chem. Soc.* (*A*), 1971, 2796.

[19] Lj. Manojlovic-Muir and K. W. Muir, *J.C.S. Dalton*, 1972, 686.

[20] See, for example, M. Laing, *Acta Cryst.*, 1978, **B34**, 2100.