Some Mononuclear Seven-co-ordinate Rhenium(III) Carbonyl Complexes; the Crystal and Molecular Structure of (2,2′-Bipyridyl)tribromodicarbonylrhenium(III)

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Treatment of *fac*-[ReX(CO)$_3$(diamine)] with halogens has afforded the seven-co-ordinate rhenium(III) complexes [ReX$_3$(CO)$_2$(diamine)] [diamine = 2,2′-bipyridyl (bipy), X = Cl or Br; diamine = 2,9-dimethyl-1,10-phenanthroline, X = Br]. Infrared evidence suggests that [ReBr$_3$(CO)$_2$(diamine)] (diamine = 1,10-phenanthroline or 2,2′-biquinolyl) and [ReBr$_3$(CO)$_2$(amine)$_2$] (amine = pyridine or 2-methylpyridine) may be formed in an analogous manner, but the desired products could not be separated from rhenium(IV) bromo-complexes also formed in the bromination reactions. Crystals of [ReBr$_3$(CO)$_2$(bipy)] are monoclinic, with a = 7.062(8), b = 14.914(8), c = 14.186(12)Å, β = 100.8(1)°, Z = 4, and space group $P2_1/c$. 1 120 Independent reflections above background have been collected on a diffractometer and refined to R 0.079. The metal atom has a distorted capped-octahedral environment in which a carbonyl group occupies the capping position [1.96(5) Å], a carbonyl group [1.96(3) Å], a nitrogen atom of the bidentate ligand [2.22(3) Å], and a bromine atom [2.635(5) Å] make up the capped face, and two bromine atoms [2.551(5) and 2.576(4) Å] and the other nitrogen atom [2.15(2) Å] complete the uncapped face.

SEVEN-CO-ORDINATION [1] has been established for a number of mononuclear rhenium(III) complexes, the most extensive group displaying this co-ordination number being more than 20 hydrido-complexes. A complete listing of these complexes may be found in ref. 1, distorted pentagonal-bipyramidal geometry having been established by *X*-ray crystallography for [ReH$_3$(dppe)$_2$] [2] and [ReH$_3$(dppe)(PPh$_3$)$_2$] [3] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$). The rhenium(III) cyclopentadienyls [Re(η-C$_5$H$_5$)$_2$H],[4] [ReMe(η-C$_5$H$_5$)X(CO)$_2$] (X = Br, I, or Me),[5] and [ReBr$_2$(η-C$_5$H$_5$)(CO)$_2$] [6] can also be regarded as seven-co-ordinate assuming the formalism that the η-C$_5$H$_5$ group occupies three co-ordination sites.

Although a considerable number of studies [1] has shown that many octahedral d^6 Group 6-substituted metal carbonyls may be oxidised by halogens to seven-co-ordinate d^4 metal carbonyl halides, similar reactions employing Group 7 metal carbonyl derivatives which would be expected to lead to seven-co-ordinate mononuclear trihalogenometal(III) complexes have been little studied. The first report [7] of such reactions indicated that [ReX(pdma)$_2$(CO)] [pdma = *o*-phenylenebis(dimethylarsine); X = Br or I] were oxidised to [ReX$_2$(pdma)$_2$(CO)]X$_3$. Only two other seven-co-ordinate rhenium(III) complexes have been prepared [8] in this manner, namely [ReCl$_3$(CO)$_2$(PMe$_2$Ph)$_2$] from either *fac*- or *mer-trans*-[ReCl(CO)$_3$(PMe$_2$Ph)$_2$] and [ReCl$_3$(CO)(PMe$_2$Ph)$_3$] from either *mer-cis*-[ReCl(CO)$_2$(PMe$_2$Ph)$_3$] or [ReCl(CO)(PMe$_2$Ph)$_4$]. The only other mononuclear seven-co-ordinate rhenium(III) complexes reported to date are [ReBr$_3$(CO)(PMe$_2$Ph)$_3$],[8] K$_4$[Re(CN)$_7$]·2H$_2$O,[9] [ReI$_3$(CNC$_6$H$_4$Me-*p*)$_4$],[10] and [Re(S$_2$CNR$_2$)$_3$(CO)] (R = Me, Et, or PhCH$_2$),[11] the diethyldithiocarbamato-complex having been shown [12] to involve a distorted pentagonal-bipyramidal geometry.

We have sought to extend the number of such complexes by examining the halogenation reactions of a group of *fac*-[ReX(CO)$_3$(diamine)] and *fac*-[ReX(CO)$_3$(amine)$_2$] complexes and report here the isolation of three complexes of the type [ReX$_3$(CO)$_2$(diamine)]. In view of the very limited number of structural studies on mononuclear seven-co-ordinate rhenium(III) complexes, we felt it to be worthwhile to determine the structure of one of these complexes by *X*-ray diffraction. The complex [ReBr$_3$(CO)$_2$(bipy)] (bipy = 2,2′-bipyridyl) was chosen for this study, an additional point of interest being the [MX$_3$(CO)$_2$(L–L)] stoicheiometry which is unusual for a seven-co-ordinate molecule. Among the multitudinous molybdenum(II) and tungsten(II) carbonyl

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halide structures [1] there are many of the types $[MX_2(CO)_2L_3]$, $[MX_2(CO)_2(L{-}L)L]$, and $[MX_2(CO)_3(L{-}L)]$ (X = Cl, Br, or I; L, L–L = uni- or bi-dentate ligands), but no examples of the type $[MX_3(CO)_2(L{-}L)]$. The geometry of $[ReBr_3(CO)_2(bipy)]$ is therefore difficult to predict, particularly since seven-co-ordinate molecules with three or four halides (Cl, Br, or I) fall into just two categories. They are known to be either pentagonal bipyramidal, as in $[WCl_4O(pdma)]$ [13] and $[NbCl_3(L{-}L)_2]$ [14] in which three halogens fit into the T formation with two in axial positions and one in an equatorial position, or alternatively capped octahedral with three halogens in the uncapped face as in $[WBr_3(CO)_4]^-$ (ref. 15) and $[MoX_4(PMe_2Ph)_3]$.[16] The former structure is impossible because the bulky bipy ligand cannot occupy an equatorial edge in a pentagonal bipyramid; the latter is unlikely because the bipy ligand would have to occupy an edge between the capping atom and an atom in the capped face and so the carbonyl groups would not be mutually *cis* as they are in nearly all the molybdenum(II) and tungsten(II) carbonyl halides.[1] We were therefore most interested to determine the structure of $[ReBr_3(CO)_2(bipy)]$ and report here the results of that investigation.

EXPERIMENTAL

Materials.—The rhenium(I) complexes *fac*-$[ReX(CO)_3(diamine)]$ [diamine = bipy, X = Cl or Br; diamine = 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (2,9Me_2-phen), or 2,2′-biquinolyl (bquin), X = Br] and *fac*-$[ReBr(CO)_3(amine)_2]$ [amine = pyridine (py) or 2-methylpyridine (2Me-py)] were prepared by treating $[ReX(CO)_5]$ with a slight excess of the amine in refluxing light petroleum (b.p. 100—120 °C) for 1 h under dry nitrogen. After cooling, the solid products were filtered off, washed with diethyl ether, and recrystallised from chloroform–diethyl ether before drying *in vacuo*. Yields were consistently >70%. Purity was established by C, H, and N analyses and i.r. ν(CO) band positions.[17]

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer, far-i.r. spectra of samples dispersed in polyethylene on a Beckman-R.I.I.C. FS 720 interferometer. Conductance measurements at 25 °C were carried out using a Wayne–Kerr autobalance bridge and a dip-type cell with platinum electrodes. Magnetic measurements were obtained by the Gouy method using $[Ni(en)_3][S_2O_3]$ (en = ethylenediamine) as calibrant.

Reactions.—Halogenations were performed under dry nitrogen employing previously dried bromine or chlorine. Subsequent manipulations were carried out in a closed vacuum system or under dry nitrogen.

(2,2′-*Bipyridyl*)*tribromodicarbonylrhenium*(III). The complex $[ReBr(CO)_3(bipy)]$ (0.35 g) was stirred at room temperature for 16 h in bromine (5 cm³). Excess of bromine was then evaporated off and the resulting deep red solid recrystallised from anhydrous chloroform (200 cm³) to give crystals suitable for an *X*-ray diffraction study, after drying *in vacuo* (yield 79%) (Found: C, 22.7; H, 1.30; N, 4.50. Calc. for $C_{12}H_8Br_3N_2O_2Re$: C, 22.6; H, 1.25; N, 4.40%).

(2,2′-*Bipyridyl*)*dicarbonyltrichlororhenium*(III). The complex $[ReCl(CO)_3(bipy)]$ (0.50 g) was stirred at room temperature in chloroform (50 cm³) and chlorine gas passed in. After a few minutes the suspension dissolved to give a red solution from which a reddish brown solid precipitated after *ca*. 10 min. This solid was filtered off, recrystallised from acetone–light petroleum (b.p. 60—80 °C), and dried *in vacuo* (yield 90%) (Found: C, 28.8; H, 1.80; N, 6.10. Calc. for $C_{12}H_8Cl_3N_2O_2Re$: C, 28.6; H, 1.60; N, 5.55%).

Tribromodicarbonyl(2,9-*dimethyl*-1,10-*phenanthroline*)-*rhenium*(III). Bromine (1.0 cm³) was added to $[ReBr(CO)_3(2{,}9Me_2\text{-phen})]$ (0.11 g) and the reaction allowed to proceed for 16 h at room temperature. Removal of excess of bromine left an orange solid which was recrystallised from anhydrous chloroform before drying *in vacuo* (yield 81%) (Found: C, 27.5; H, 1.55; N, 4.35. Calc. for $C_{16}H_{10}Br_3N_2O_2Re$: C, 27.9; H, 1.45; N, 4.05%).

Other bromination reactions attempted are mentioned in the Results and Discussion section.

Crystal Data.—$C_{12}H_8Br_3N_2O_2Re$, $M = 637.9$, Monoclinic, $a = 7.062(8)$, $b = 14.914(8)$, $c = 14.186(12)$ Å, $\beta = 100.8(1)°$, $U = 1\,467.6$ Å³, $D_c = 2.88$, $Z = 4$, $D_m = 2.80(5)$ g cm^{-3}, λ(Mo-K_α) = 0.710 7 Å, $\mu = 169.0$ cm^{-1}, $F(000) = 1\,160$, space group $P2_1/c$ from systematic absences $0k0$ where $k = 2n + 1$ and $h0l$ where $l = 2n + 1$.

A crystal with dimensions 0.25 × 0.15 × 0.30 mm was mounted with the a^* axis parallel to the instrument axis of a General Electric XRD5 apparatus which was used to measure diffraction intensities (*via* the stationary-crystal–stationary-counter method) and cell dimensions (*via* least-squares refinement of high-angle reflections). It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken as a function of 2θ. No crystal decay was observed. 2 362 Independent reflections were measured with $2\theta < 50°$ of which 1 120 with $I > 1.5\sigma(I)$ were used in subsequent calculations. An absorption correction was applied with the program ABSORB.[17]

Structure Determination.—The positions of the metal atom were found from a Patterson map. Successive Fourier maps gave the positions of the remaining atoms in the molecule. The structure was refined, with Re and Br anisotropic, O, N, and C isotropic, by full-matrix least squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $(\sin\theta)/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 140$ and $w^{\frac{1}{2}} = 140/F_o$ for $F_o > 140$. Calculations were made on a C.D.C. 7600 computer at the University of London Computer Centre using the '*X*-RAY' system of programs.[18] Atomic scattering factors and corrections for anomalous dispersion were taken from ref. 19. In the final cycle of refinement no shift was >0.1 σ and R was 0.079. There were no significant peaks in the final difference-Fourier map. The reflections

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with zero weighting showed no large discrepancies. Positional co-ordinates are given in Table 1 and molecular dimensions in Table 2. Thermal parameters, observed and calculated structure factors, and intermolecular distances < 3.6 Å are listed in Supplementary Publication No. SUP 22280 (8 pp.).*

TABLE 1

Final positional parameters (× 10^4) for [$ReBr_3(CO)_2$(bipy)]

Atom	*x*	*y*	*z*
Re	3 850(2)	2 067(1)	0 335(1)
Br(1)	1 426(8)	3 349(3)	0 589(3)
Br(2)	6 698(6)	1 361(3)	−0 262(3)
Br(3)	3 184(7)	2 834(3)	−1 320(3)
C(1)	1 936(71)	1 673(30)	1 080(33)
O(1)	0 933(59)	1 386(26)	1 521(30)
C(2)	2 298(46)	1 135(19)	−0 429(22)
O(2)	1 511(51)	0 632(21)	−0 887(24)
N(1)	5 950(49)	3 109(20)	0 972(23)
N(2)	5 430(48)	1 437(21)	1 603(23)
C(3)	6 101(54)	3 888(24)	0 684(25)
C(4)	7 206(71)	4 558(29)	1 141(33)
C(5)	8 289(64)	4 309(28)	2 061(28)
C(6)	8 176(60)	3 507(24)	2 433(28)
C(7)	6 956(53)	2 863(24)	1 857(24)
C(8)	6 773(49)	1 997(23)	2 197(23)
C(9)	7 911(59)	1 608(25)	3 023(27)
C(10)	7 663(71)	0 739(31)	3 256(31)
C(11)	6 475(56)	0 195(23)	2 609(26)
C(12)	5 330(58)	0 549(24)	1 853(26)

TABLE 2

Molecular dimensions (distances in Å, angles in °)

Re–C(1)	1.96(5)	C(1)–Re–C(2)	73.4(16)
Re–C(2)	1.96(3)	C(1)–Re–N(1)	117.8(16)
Re–N(1)	2.22(3)	C(1)–Re–N(2)	73.7(15)
Re–N(2)	2.15(2)	C(1)–Re–Br(1)	67.2(13)
Re–Br(1)	2.635(5)	C(1)–Re–Br(2)	136.3(13)
Re–Br(2)	2.551(5)	C(1)–Re–Br(3)	126.9(13)
Re–Br(3)	2.576(4)	C(2)–Re–N(1)	168.7(14)
C(1)–O(1)	1.12(6)	C(2)–Re–N(2)	107.5(12)
C(2)–O(2)	1.08(4)	C(2)–Re–Br(1)	106.2(9)
N(1)–C(3)	1.24(5)	C(2)–Re–Br(2)	85.3(10)
N(1)–C(7)	1.37(4)	C(2)–Re–Br(3)	79.8(9)
N(2)–C(8)	1.42(4)	N(1)–Re–N(2)	76.3(9)
N(2)–C(12)	1.37(4)	N(1)–Re–Br(1)	80.7(9)
C(3)–C(4)	1.36(7)	N(1)–Re–Br(2)	85.2(9)
C(4)–C(5)	1.43(6)	N(1)–Re–Br(3)	93.1(8)
C(5)–C(6)	1.31(6)	N(2)–Re–Br(1)	116.9(5)
C(6)–C(7)	1.44(5)	N(2)–Re–Br(2)	77.2(7)
C(7)–C(8)	1.39(5)	N(2)–Re–Br(3)	159.3(8)
C(8)–C(9)	1.42(5)	Br(1)–Re–Br(2)	156.5(2)
C(9)–C(10)	1.36(5)	Br(1)–Re–Br(3)	77.9(2)
C(10)–C(11)	1.38(5)	Br(2)–Re–Br(3)	84.3(2)
C(11)–C(12)	1.33(5)	Re–C(1)–O(1)	174(4)
		Re–C(2)–O(2)	175(3)
Re–N(1)–C(3)	128(3)	Re–N(2)–C(8)	115(2)
Re–N(1)–C(7)	112(2)	Re–N(2)–C(12)	126(2)
C(3)–N(1)–C(7)	119(3)	C(8)–N(2)–C(12)	118(2)
N(1)–C(3)–C(4)	126(4)	N(2)–C(8)–C(7)	116(3)
C(3)–C(4)–C(5)	114(6)	N(2)–C(8)–C(9)	118(3)
C(4)–C(5)–C(6)	123(4)	C(7)–C(8)–C(9)	126(3)
C(5)–C(6)–C(7)	117(3)	C(8)–C(9)–C(10)	120(3)
C(6)–C(7)–N(1)	120(3)	C(9)–C(10)–C(11)	119(4)
C(8)–C(7)–N(1)	120(3)	C(10)–C(11)–C(12)	120(3)
C(6)–C(7)–C(8)	120(3)	N(2)–C(11)–C(12)	122(3)

RESULTS AND DISCUSSION

When [$ReCl(CO)_3$(bipy)] is treated with chlorine in chloroform or [$ReBr(CO)_3$(bipy)] and [$ReBr(CO)_3$(2,9-Me_2-phen)] are treated with anhydrous bromine at room temperature the products are the seven-co-ordinate rhenium(III) complexes of general formula [$ReBr_3(CO)_2$(diamine)]. The [$ReX_3(CO)_2$(L–L)] stoicheiometry is novel, the closely related [$ReX_3(CO)_2L_2$] being known for only one example,[8] that with L = PMe_2Ph. The three products are diamagnetic at room temperature and non-conducting in acetonitrile. These halogenation reactions therefore fit into the pattern so well established for substituted Group 6 metal carbonyls where the octahedral d^6 complexes are oxidised to afford seven-co-ordinate d^4 complexes, in accordance with the 18-electron formalism.

The three complexes each display (Table 3) two i.r. ν(CO) bands at quite similar frequencies to those reported [8] for [$ReCl_3(CO)_2(PMe_2Ph)_2$]. An examination of the mid- and far-i.r. spectra of the two bipy complexes shows that at <600 cm^{-1} the spectra contain several bands common to both complexes, presumably associated with co-ordinated bipy, δ(ReCO) and ν(ReC) vibrations, as well as some unique intense absorptions (Table 3) which can be attributed to rhenium–halogen stretching vibrations. The mean ν(ReBr)/ν(ReCl) value of 0.73 falls within the expected ν(MBr)/ν(MCl) range of 0.65—0.85, giving some support to these assignments. Additional bands at 266 cm^{-1} for the chloro-complex and 273 cm^{-1} for the bromo-complex may be tentatively assigned to vibrations involving significant rhenium–nitrogen stretching character in line with such assignments [20] for other transition-metal bipy complexes.

TABLE 3

Infrared data (cm^{-1})

Complex	ν(CO)(Nujol)	ν(ReX)	ν(ReN)
[$ReCl_3(CO)_2$(bipy)]	1 995s, 1 922s	320s, 312s, 298s	266ms
[$ReBr_3(CO)_2$(bipy)]	2 020s, 1 930s	247s, 232s, 203s	273s
[$ReBr_3(CO)_2$(2,9Me_2-phen)]	2 000s, 1 920s		

Bromination reactions carried out in an analogous manner employing [$ReBr(CO)_3$(L–L)] (L–L = phen or bquin) or [$ReBr(CO)_3L_2$] (L = py or 2Me-py) led to mixtures of products which could not be effectively separated. However, analytical results, together with i.r. and magnetic measurements, suggest the products to contain the desired [$ReBr_3(CO)_2$(L–L)] or [$ReBr_3(CO)_2L_2$] complexes mixed with carbonyl-free octahedral paramagnetic rhenium(IV) bromo-complexes. Attempts to moderate the reaction conditions in order to avoid this exhaustive bromination [*e.g.* by the use of bromine in light petroleum (b.p. 100—120 °C), lower temperatures,

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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or shorter reaction times] led to mixtures containing significant amounts of the rhenium(I) starting materials.

The tribromo-complex $[\mathrm{ReBr_3(CO)_2(bipy)}]$ has been subjected to a single-crystal *X*-ray diffraction study. The discrete molecule is shown in Figure 1. The metal atom is seven-co-ordinate with a distorted capped octahedral environment. A carbonyl group occupies the capping position [Re–C(1) 1.96(5) Å], a carbonyl group, a bromine atom, and a nitrogen atom the capped face [Re–C(2) 1.96(3), Re–Br(1) 2.635(5), and Re–N(1) 2.22(3) Å], and two bromine atoms and the other nitrogen atom the uncapped face [Re–Br(2) 2.551(5), Re–Br(3) 2.576(4), and Re–N(2) 2.15(2) Å]. The structure is therefore similar to those of the many molybdenum(II) complexes listed in ref. 1. The vast majority of these have capped octahedral structures with carbonyl groups in the capping position and the capped face, halogens in the uncapped face, and bidentate ligands filling an edge between sites in the capped and uncapped faces.

These features are also found in the present molecule but only because the Br(1) atom occupies a unique position for such an atom, namely a site in the capped face. The Br(1)–Re–Br(3) angle is only 77.9(2)° (a normal angle for this edge), which gives a Br(1) · · · Br(3) distance of 3.29 Å. This is a remarkably short distance and would be even shorter were it not that the Re–Br(1) bond and to a lesser extent the Re–Br(3) bond are lengthened from the value found for the relatively uncrowded Re–Br(2) bond. Because of the paucity of data on $\mathrm{Re^{III}}$–Br bond lengths it is difficult to judge whether this Re–Br(2) bond length [2.551(5) Å] is normal. However, it is certainly much longer than the 2.447 Å established for terminal Re–Br bonds in the isolated $\mathrm{Re_3Br_9}$ unit found[21] within $\mathrm{[Hquin]_2[Re_4Br_{15}]}$ (Hquin = quinolinium), the 2.37—2.49 Å range found for terminal Re–Br bonds in $\mathrm{Cs_2[Re_3Br_{11}]}$,[22] and the average terminal Re–Br bond length (2.478 ± 0.006 Å) found for $\mathrm{Cs_2[Re_2Br_8]}$,[23] although, of course, each of these examples are metal–metal-bonded systems.

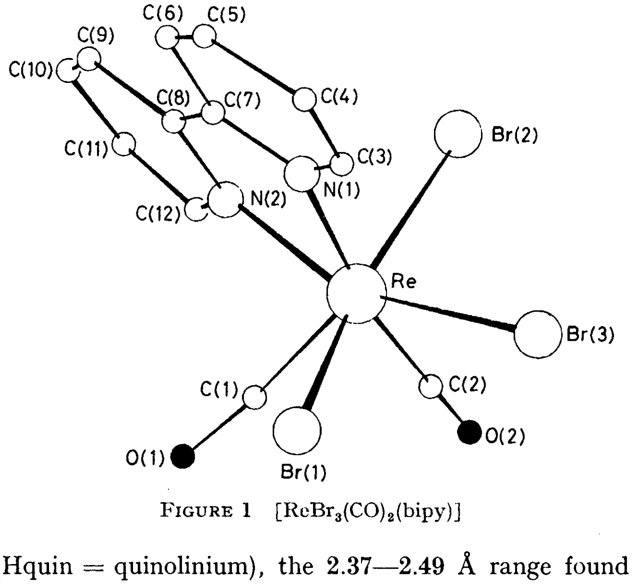

FIGURE 1 $[\mathrm{ReBr_3(CO)_2(bipy)}]$

It has been suggested[1] that in seven-co-ordinate complexes containing halides (Cl, Br, or I) the requirement that these atoms be at least 90° away from each other is an all-important factor in the choice of geometry. Before the present structure determination the only exception to this theory was provided by $[\mathrm{WCl_4O(pdma)}]$[12] and it was argued in this example that the terminal oxygen atom takes precedence over the halogens and forces them into the cramped pentagonal girdle. The complex $[\mathrm{ReBr_3(CO)_2(bipy)}]$ provides a more surprising exception. Clearly the most favourable structure for a $\mathrm{M(L{-}L)L_5}$ molecule from an energetic standpoint is the capped octahedron with the bidentate ligand in an edge between the capped and uncapped faces, and this allied to the carbonyl groups remaining mutually *cis* is sufficient to overcome the positioning of Br(1) in such a cramped position. Steric repulsions are somewhat lessened in this arrangement by Br(1) and Br(2) being mutually *trans*.

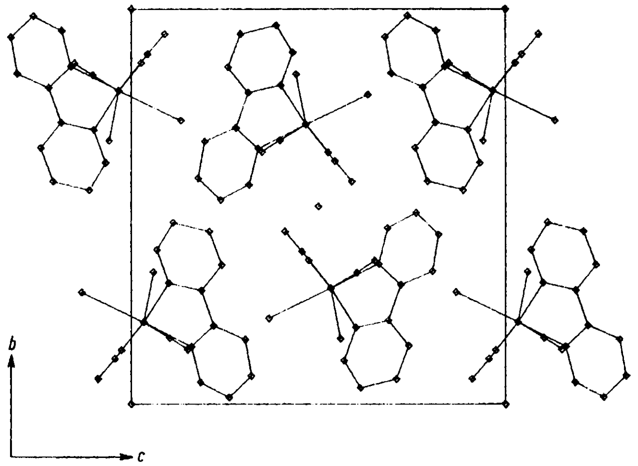

FIGURE 2 Unit cell of $[\mathrm{ReBr_3(CO)_2(bipy)}]$

One of us has shown previously[1] that the effect of introducing a bidentate ligand into a capped octahedron is to distort that polyhedron towards a capped trigonal prism. The present molecule provides further evidence for this in that the δ' angles (after normalisation) are 0.2, 19.2, and 26.5° for $[\mathrm{ReBr_3(CO)_2(bipy)}]$ compared to ideal values[24] for the capped octahedron of 16.2, 16.2, and 16.2° and for the capped trigonal prism of 0, 0, and 41.5°. Root-mean-square deviations[1] from the two ideal geometries are 0.068 Å from the capped octahedron and 0.103 Å from the capped trigonal prism [with Br(1) capping].

The two heterocyclic rings of the bipy ligand are planar to within experimental error and intersect at an angle of 7.7°. The rhenium atom is 0.14 and −0.24 Å

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from the two planes. Re–N, Re–C, and C–O distances are as expected; the Re–C distances (each of 1.96 Å), may be compared with 1.852 Å found [12] for pentagonal-bipyramidal [Re(S_2CNEt_2)$_3$(CO)].

The packing diagram in the *a* projection is given in Figure 2. There are no intermolecular distances significantly less than the sum of the van der Waals radii.

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