Crystal and Molecular Structures of Potassium Pentachloro- and Pentabromo-nitrosyliridate Hydrate

By **Frank Bottomley**, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

The crystal and molecular structures of the title compounds [Cl (I), Br (II)] have been investigated by use of diffractometer data. The compounds are isomorphous and isostructural, orthorhombic, space group *Pnma* or $Pn2_1a$, $Z = 4$; (I), $a = 22.416(5)$, $b = 6.935(1)$, $c = 6.069(1)$ Å; (II), $a = 23.272(9)$, $b = 7.261(5)$, $c = 6.302(3)$ Å. The structures were solved by the heavy-atom method and refined by full-matrix methods to R 0.049 [(I), 1 704 reflections] and 0.096 [(II), 1 291 reflections]. The iridium atom is octahedrally co-ordinated by five halide ions and the nitrogen atom of the NO ligand. Both structures show the *trans*-shortening influence of NO when co-ordinated formally as NO^+. For (I) Ir–Cl(eq) distances are 2.335(2) and 2.342(2), and Ir–Cl(ax) 2.286(3) Å; for (II) the analogous distances are 2.475(3) and 2.485(3), and 2.419(4) Å. Ir–N and N–O distances and Ir–N–O angles are for (I) 1.76(1) and 1.12(2) Å, and 174.3(1)°, and for (II) 1.71(2) and 1.17(4) Å, and 170.3(3)°.

In a previous paper on nitrosyls of ruthenium ammines I indicated interest in the structures of those nitrosyl complexes which are reactive towards nucleophiles.[1] I wish to correlate the electrophilic behaviour of co-ordinated NO (co-ordinated formally as NO^+) to the structural parameters of its complexes, and to investigate the *trans*-influence of co-ordinated NO^+. The complexes $K[IrCl_5NO]\cdot H_2O$ (I) and $K[IrBr_5NO]\cdot H_2O$ (II) are very reactive towards nucleophiles, and they have different equilibrium constants for their reaction with OH^-.[2] They also contain identical axial and equatorial ligands, and therefore have the internal standard necessary for an unambiguous assessment of the *trans*-influence of NO^+. These complexes are therefore ideal for my interests, and their structures are reported here.

EXPERIMENTAL

Complexes (I) and (II) were prepared by the literature method.[2] Suitable crystals of (II) were obtained by setting aside a saturated solution of the complex in concentrated hydrobromic acid for several days at 5 °C. Crystals were mounted in thin-walled glass tubes for *X*-ray measurements. Weissenberg photographs (Cu-K_α radiation) of the $h0$—$4l$ layers showed systematic absences and symmetry in agreement with the orthorhombic space groups *Pnma* (D_{2h}^{16}, No. 62) or $Pn2_1a$ (non-standard setting of $Pna2_1$ (C_{2v}^{9}, No. 33)). The former was used in the structure refinement, though a good case can be made for the latter as the correct space group (*vide infra*).

Crystal Data.—(II), $Br_5H_2IrKNO_2$, $M = 687.9$, Orthorhombic, $a = 23.272(9)$, $b = 7.261(5)$, $c = 6.302(3)$ Å, $U = 1\,064.9$ Å^3. $D_c = 4.29$, $Z = 4$. Mo-$K_{\alpha1}$ radiation, $\lambda = 0.709\,26$ Å; μ (Mo-K_α) = 334.6 cm^{-1}. D_c is reasonable for this type of complex. No liquid with a sufficiently high density could be found to determine D_m.

On setting aside a saturated solution of (I) in concentrated hydrochloric acid at 5 °C, well-formed crystals were deposited. However, photographic examination showed these were face-centred cubic and of *m3m* symmetry ($a = 6.98$ from uncalibrated photographs). These crystals were not further investigated since it seemed highly probable that they had a disordered structure. Crystals of (I) which were isomorphous with those of (II) were obtained by setting aside a saturated solution of (I) in concentrated hydrochloric acid at −35°C for several weeks.

Crystal Data.—(I), $Cl_5H_2IrKNO_2$, $M = 456.6$, $a = 22.416(5)$, $b = 6.935(1)$, $c = 6.069(1)$ Å, $U = 943.4$ Å^3, $D_c = 3.21$, $Z = 4$. μ(Mo-K_α) = 168.1 cm^{-1}.

Collection and Reduction of Intensity Data.—The crystal of (I) used for the determination of intensities was a needle (*ca.* 0.16 × 0.8 × 0.08 mm) and was mounted with the needle axis (b) *ca.* 8° mis-set from the ϕ axis of a Picker FACS 1 diffractometer.[3] A needle of (II) (0.08 × 1.0 × 0.12 mm) was similarly mounted. Cell dimensions were determined from 12 accurately centred reflections with $2\theta > 50°$ for (I) and $> 40°$ for (II). For (I) a unique hkl data set was collected to 2θ 65° (1 832 reflections) and for (II) to 60° (1 679 reflections) by the ω—2θ scan technique. Instrument settings were basically as described previously,[4] with the exception that the diffractometer is now equipped with a graphite monochromator and that because of severe reflection overlap at high 2θ (due to the large a cell dimension) the counter aperture was reduced to *ca.* 0.5 cm in width. Three standard reflections, monitored every 50 reflections, showed no significant changes for (I) or (II).

Absorption, Lorentz, and polarisation corrections were

---

[1] F. Bottomley, *J.C.S. Dalton*, 1974, 1600.

[2] F. Bottomley, S. G. Clarkson, and S. B. Tong, *J.C.S. Dalton*, 1974, 2344.

[3] W. H. Zachariasen, *Acta Cryst.*, 1965, **18**, 705.

[4] F. Bottomley, *J.C.S. Dalton*, 1972, 2148.

applied to the data [μR 5.5—25.1 for (I), and 3.5—12.5% for (II)].[5] Reflections with a net count <10 or <0.05 times background were considered unobserved and not used in the structure refinements. The structure of (I) was solved from 1 672 observed structure amplitudes, and that of (II) from 1 291.

Structure Solution and Refinement.—The structures of (I) and (II) were solved in parallel by use of standard Patterson, isomorphous replacement, and Fourier techniques. The scattering factor curve for Ir^{4+} was taken from ref. 6 and those for Br^-, Cl^-, N, and O from ref. 7; those for Ir^{4+}, Br^-, and Cl^- were corrected for both the real and imaginary parts of the anomalous dispersion. Refinement was by the full-matrix method, the function minimised being $\Sigma w(|F_o| - |F_c|)^2$. Weighting schemes of the form $w = 1/(a + F_o + BF_o^2 + CF_o^3)$, where $A = 14$, $B = 3.9 \times 10^{-3}$, and $C = 1.9 \times 10^{-5}$ for (I) and $A = 28$, $B = 3.3 \times 10^{-3}$, and $C = 1.38 \times 10^{-5}$ for (II) were used. With the Ir, Cl, or Br, and K atoms given anisotropic thermal parameters and N and O isotropic, refinements of both structures in space group *Pnma* proceeded normally to convergence at R 0.049 (R' 0.080) for (I) and 0.096 (R' 0.10) for (II), where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. An extinction parameter was included in the last cycles of refinement.

At this stage various tests were made. There was no significant decrease in R or R' when the light atoms were allowed to vibrate anisotropically. Refinement of (I) in the non-centric $Pn2_1a$ space group gave R 0.044 (R' 0.067). This decrease is significant at >0.005 confidence level according to Hamilton's test.[8] However, the validity of this test has been questioned in cases where there are serious correlation problems.[9,10] These occur in the $Pn2_1a$ refinement, correlation coefficients of up to 0.88 being found between the parameters of the four equatorial chlorine atoms. As a result the Ir–Cl bond distances for these four chemically equivalent atoms differed by up to 0.1 Å, though the mean was identical to that from the *Pnma* refinement, and none of the other bond distances or angles were significantly different. An E statistics test favoured the non-centric $Pn2_1a$ also, though not strongly. However, because of the correlation problem it was decided to accept the *Pnma* refinement, recognising that the errors quoted may be too small.[10] The situation was similar for (II), except that the E statistics test here favoured the centric *Pnma*, again not strongly. Again, *Pnma* was accepted.

TABLE 1

Positional and thermal * parameters for (I)

Atom	x	y	z	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Ir	0.12662(1)	0.25	0.11445(6)	208(2)	163(2)	295(3)	0	−8(1)	0
Cl(1)	0.19345(10)	0.0137(3)	−0.0046(4)	349(9)	282(9)	530(12)	80(7)	15(8)	−92(8)
Cl(2)	0.06381(9)	0.0110(3)	0.2575(4)	376(10)	280(9)	494(11)	−127(7)	20(8)	63(8)
Cl(3)	0.17607(13)	0.25	0.4439(5)	288(12)	408(15)	355(13)	0	−67(10)	0
K	0.32342(16)	0.25	−0.0092(7)	462(17)	377(15)	701(23)	0	−49(16)	0
				10^3U					
N	0.0843(5)	0.25	−0.1299(17)	33(2)					
O(1)	0.0532(5)	0.25	−0.2753(24)	56(3)					
O(2)	0.4205(6)	0.25	0.2533(29)	67(3)					

* The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$, and $\exp[-8\pi^2(\sin\theta/\lambda)^2U]$ for the isotropic.

TABLE 2

Positional and thermal * parameters for (II)

Atom	x	y	z	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Ir	0.12598(5)	0.25	0.1377(2)	201(6)	234(6)	221(6)	0	−6(4)	0
Br(1)	0.1951(1)	0.0118(4)	0.0201(4)	382(13)	363(13)	423(14)	116(10)	−2(10)	−82(11)
Br(2)	0.0603(1)	0.0106(4)	0.2812(5)	410(14)	439(15)	511(16)	166(12)	−15(12)	93(14)
Br(3)	0.1752(1)	0.25	0.4758(6)	310(16)	384(18)	267(15)	0	−52(12)	0
K	0.3263(4)	0.25	0.0131(20)	419(47)	430(48)	669(69)	0	−33(46)	0
				10^3U					
N	0.0872(10)	0.25	−0.0927(40)	20(4)					
O(1)	0.0539(13)	0.25	−0.2312(56)	47(7)					
O(2)	0.4211(16)	0.25	0.2748(60)	54(8)					

* See footnote to Table 1.

No attempt was made to locate the hydrogen atoms of the water of crystallisation. On the final cycles no shift was $>0.01\sigma$ for (I) or $>0.02\sigma$ for (II). Difference-Fourier syntheses showed maxima and minima of 3.5 and −2.7 for (I) and 6.8 and -4.9 eÅ^{-3} for (II); in both cases negative and positive peaks were <1 Å from the Ir atom. No other significant peaks were found for either structure. An error analysis showed poor agreement for the $0kl$ reflections in both cases, but deletion of these reflections and re-refinement gave no change in R or R', nor were the parameters significantly affected. The estimated standard deviation of an observation of unit weight was 0.41 electrons for (I) and 0.85 for (II). Tables 1 and 2 give the parameters and standard deviations from the last cycle for (I) and (II) respectively (the numbering scheme is shown in the Figure).

---

[5] Computer programs used in this work were: PICKERA, a locally modified version of the data reduction programme written by F. R. Ahmed, National Research Council, Ottawa, Canada; '*X*-Ray' system, Technical Report TR 192, Computer Science Center, University of Maryland, June 1972.

[6] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

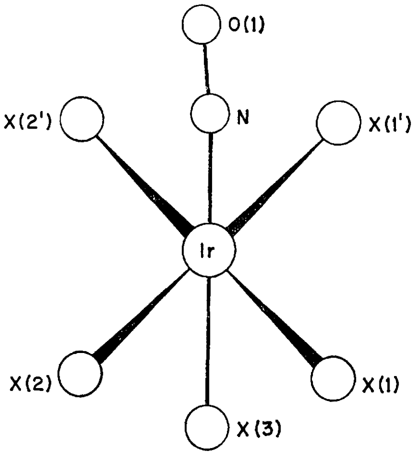
[7] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

[8] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[9] A. Whitaker and J. W. Jeffrey, *Acta Cryst.*, 1967, **23**, 984.

[10] Y. P. Jeannin and D. R. Russell, *Inorg. Chem.*, 1970, **9**, 778.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21505 (28 pp., 1 microfiche).*



Numbering scheme for the $[IrX_5NO]^-$ anion (X = Cl or Br)

DISCUSSION

The structures consist of well separated K^+ cations, $[IrX_5NO]^-$ anions, and water of crystallisation. The shortest cation–anion distance in (I) is 3.34 Å [K · · · Cl(1)] and the shortest distance involving the water oxygen is 3.47 Å [O(2) · · · Cl(1)]. For (II) these same distances are 3.51 [K · · · Br(1)] and 3.65 Å [O(2) · · · Br(1)]. The nitrosyl oxygen atom [O(1)] is 3.24 Å from the *trans*-Cl [Cl(3)] of an adjacent anion in (I) and 3.37 Å from Br(3) in (II). Hence hydrogen bonding must be weak and distortions of the anions due to non-bonded interactions very small. Inspection of the distances (uncorrected) and angles (Table 3) and a selection of weighted mean planes (Table 4) for (I) shows distortions of the anion from idealised C_{4v} symmetry are small [strict C_s symmetry is crystallographically imposed by a plane through Cl(3), Ir, N, and O(1), bisecting Cl(1) · · · Cl(1′) and Cl(2) · · · Cl(2′) (see Figure)]. The distortions are mainly in the Ir–N–O and Cl(3)–Ir–N angles. Tables 5 and 6 give the same information for (II), and the same, but rather larger, deviations from C_{4v} symmetry are observed. In both cases the equatorial halides are bent away from NO^+ [0.08 Å in (I) and 0.09 Å in (II)].

TABLE 3

Intramolecular geometry in the anion of (I)

(*a*) Distances (Å)

Ir–Cl(1)	2.335(2)	Ir–N	1.760(11)
Ir–Cl(2)	2.342(2)	N–O(1)	1.124(17)
Ir–Cl(3)	2.286(3)		

(*b*) Angles (°)

N–Ir–Cl(1)	94.9(3)	Cl(1)–Ir–Cl(1′)	89.15(8)
N–Ir–Cl(2)	89.3(3)	Cl(1)–Ir–Cl(3′)	175.8(2)
N–Ir–Cl(3)	176.4(3)	Cl(2)–Ir–Cl(3)	88.13(8)
Cl(1)–Ir–Cl(2)	90.21(8)	Cl(2)–Ir–Cl(2′)	90.12(7)
Cl(1)–Ir–Cl(3)	87.68(8)	Ir–N–O(1)	174.3(1.1)

The mean Ir–Cl(eq) distance in the anion of (I) is $2.338_5(2)$ and the Ir–Cl(ax) distance 2.286(3) Å. This confirms the suggestion, originally made by Veal and Hodgson,[11] from a study of $[RuCl_5NO]^{2-}$, that when the good π-acceptor but poor σ-donor ligand NO^+ is *trans* to a good σ-donor ligand such as Cl^- a short M–X bond *trans* to NO^+ will result. Previous attempts to confirm this idea unambiguously have been only partially successful,[1] but the 0.05 Å difference observed here is even more marked than the 0.02 Å difference for $[RuCl_5NO]^{2-}$.[11] The ability of NO^+ to withdraw electrons from iridium by π-bonding and hence to shorten the other ligand distances is further illustrated when the present Ir–Cl distances are compared with previously found distances. For a wide variety of six-co-ordinate, formally Ir^{III}, complexes (many containing π-acceptor groups such as CO or R_3P) the Ir–Cl distances are in the range 2.35—

TABLE 4

Equations * of weighted mean planes and, in square brackets, distances (Å) of atoms from the plane for the anion of (I)

Plane (1): Ir, Cl(1), Cl(1′), Cl(2), Cl(2′)

$$0.4801X + 0.8772Z = 2.0405$$

[Ir −0.068, Cl(1), 0.017, Cl(2) 0.017]

Plane (2): Ir, Cl(1), Cl(2′), Cl(3), N

$$0.6080X + 0.7089Y - 0.3575Z = 2.6924$$

[Ir 0.014, Cl(1) 0.022, Cl(2′) 0.023, Cl(3) −0.026, N −0.132, O(1) −0.141]

* *X*, *Y*, and *Z* are orthogonal co-ordinates in Å, related to the crystallographic axes by: $X = ax$, $Y = by$, and $Z = cz$.

TABLE 5

Intramolecular geometry in the anion of (II)

(*a*) Distances (Å)

Ir–Br(1)	2.475(3)	Ir–N	1.710(25)
Ir–Br(2)	2.485(3)	N–O(1)	1.166(42)
Ir–Br(3)	2.419(4)		

(*b*) Angles (°)

N–Ir–Br(1)	95.09(59)	Br(1)–Ir–Br(1′)	88.67(10)
N–Ir–Br(2)	89.09(59)	Br(1)–Ir–Br(2′)	175.81(15)
N–Ir–Br(3)	176.4(9)	Br(2)–Ir–Br(3)	88.32(10)
Br(1)–Ir–Br(2)	91.13(10)	Br(2)–Ir–Br(2′)	88.77(11)
Br(1)–Ir–Br(3)	87.49(9)	Ir–N–O(1)	170.3(2.6)

TABLE 6

Equations * of weighted mean planes and, in square brackets, distances (Å) of atoms from the plane for the anion of (II)

Plane (1): Ir, Br(1), Br(1′), Br(2), Br(2′)

$$0.4647X + 0.8855Z = 2.2035$$

[Ir −0.072, Br(1) 0.018, Br(2) 0.018]

Plane (2): Ir, Br(1), Br(2′), Br(3), N

$$0.6083X + 0.7144Y - 0.3458Z = 2.7622$$

[Ir 0.018, Br(1) 0.016, Br(2′) 0.017, Br(3) −0.022, N −0.029, O(1) −0.198]

* See footnote to Table 4.

---

* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

[11] J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 1420.

2.52 Å.[12-21] The complex most nearly comparable to (I) is $K[IrCl_5(C_4H_4N_2)]\cdot 1/2H_2O$, for which the mean Ir–Cl(eq) distance is 2.351(3) and Ir–Cl(ax) 2.379(2) Å.[12] The Ir–Cl(ax) distance in (I) [2.286(3) Å] is the shortest Ir^{III}–Cl distance yet observed, and is in fact 0.03 Å shorter than the Ir^{IV}–Cl distance [2.324(5) Å] in $[IrCl_4(PMe_2Ph)_2]$.[18] Structures containing Ir–Br bonds are too scarce to reinforce the argument by comparison with the structure of (II), but the 0.06 Å difference between the mean Ir–Br(eq) [2.480(3) Å] and Ir–Br(ax) [2.419(4) Å] distances provides further confirmation of the *trans*-shortening influence of co-ordinated NO^+.

There does not appear to be any previous structural information on six-co-ordinate iridium(III) nitrosyls. The Ir–N and N–O distances, and Ir–N–O angles for (I) and (II), are in the same ranges as observed for other complexes [22-28] containing the IrNO moiety when this is approximately linear. The short NO distance in (I) may reflect its extremely high stretching frequency (2 008 cm^{-1}). The Ir–N and N–O distances in (I) and (II) follow the trend expected from their ν(NO) values, *i.e.* back donation *via* π-bonding is greater in (II) than (I), resulting in a shorter M–N and longer N–O distance. However, the errors are such, particularly for (II) (where the absorption coefficient is so high that any minor imperfections of the crystal or errors in determining its dimensions will produce large errors in the structure amplitudes) that the differences are only marginally significant. The Ir–N–O angles are reasonable close to 180°, and because of the errors the deviations from linearity (which should not be found for complexes of strict C_{4v} symmetry [29,30]) are again only marginally significant.

I thank Dr. H. Lynton for the use of the *X*-ray facilities, Dr. P. White for helpful discussions and assistance with computor programmes, Dr. S. G. Clarkson for samples of (I) and (II), Johnson, Matthey for a generous loan of iridium, and the National Research Council of Canada for financial support.

[5/796 *Received, 28th April*, 1975]

---

[12] J.-J. Bonnet and Y. Jeannin, *J. Inorg. Nuclear Chem.*, 1973, **35**, 4103.

[13] A. J. Schultz, G. P. Khare, C. D. Mayer, and R. Eisenberg, *Inorg. Chem.*, 1974, **13**, 1019.

[14] R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, 1972, **11**, 2237.

[15] M. McPartlin and R. Mason, *J. Chem. Soc.* (*A*), 1970, 2206.

[16] J. A. Ibers, D. S. Hamilton, and W. H. Baddley, *Inorg. Chem.*, 1973, **12**, 229.

[17] J. M. Guss and R. Mason, *J.C.S. Dalton*, 1972, 2193.

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

[19] A. J. Schultz, G. P. Khare, J. V. McArdle, and R. Eisenberg, *J. Amer. Chem. Soc.*, 1973, **95**, 3434.

[20] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1035.

[21] F. W. B. Einstein and D. Sutton, *J.C.S. Dalton*, 1973, 434.

[22] G. R. Clark, J. M. Waters, and K. R. Whittle, *Inorg. Chem.*, 1974, **13**, 1628.

[23] C. Pratt Brock and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 2812.

[24] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 1105.

[25] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1479.

[26] V. G. Albano, P. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 2420.

[27] P.-T. Cheng and S. C. Nyburg, *Inorg. Chem.*, 1975, **14**, 327.

[28] M. Angoletta, G. Ciani, M. Manassero, and M. Sansoni, *J.C.S. Chem. Comm.*, 1973, 789.

[29] S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1661.

[30] J. H. Enemark, *Inorg. Chem.*, 1971, **10**, 1952.