

and 1.38 (1) Å found for the corresponding distances in the arylimino complexes. One would expect a longer bond here since the radius of  $sp^3$ -hybridized carbon is larger than that of  $sp^2$ -hybridized carbon. It does, however, compare well with the distance 1.42 Å reported for the N-CH<sub>3</sub> bond in methyl isocyanide.<sup>19</sup>

The Re-N-CH<sub>3</sub> angle is close to linearity at 173 (1)°. This compares well with the corresponding angles in the arylimino complexes (see Table VII) and suggests that, as originally proposed by Chatt and coworkers,<sup>1</sup> the Re-N bond has considerable triple-bond character or at least confirms that the N atom is formally  $sp$  hybridized in the complexes so that its orbitals are in a suitable configuration for formation of a triple bond.

(19) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1968).

The Re-N distance in the present structure is 1.685 (11) Å. This bond length is very similar to those found in the other complexes and thus the Re-N bond length appears to be largely independent of the group attached to N. This observation, although surprising, is at least consistent with our previous findings that the Re-N bond length is unexpectedly insensitive to change of the *para* substituent on the arylimino ring. The bonding in this compound will be further discussed in the following paper<sup>18</sup> which describes the structure of the six-coordinate nitrido complex anion OsNCl<sub>5</sub><sup>2-</sup>.

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## Studies of Metal-Nitrogen Multiple Bonds. V. The Crystal Structure of Potassium Nitridopentachloroosmate(VI), K<sub>2</sub>OsNCl<sub>5</sub>

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The crystal structure of potassium nitridopentachloroosmate(VI), K<sub>2</sub>OsNCl<sub>5</sub>, has been determined from three-dimensional X-ray data collected by counter methods and has been refined by least-squares techniques to a final *R* factor, based on *F*, of 3.3% for the 687 reflections above background. The material crystallizes in space group D<sub>2h</sub><sup>16</sup>-Pnma of the orthorhombic system in a cell with dimensions *a* = 13.27 (2) Å, *b* = 9.85 (1) Å, and *c* = 6.84 (1) Å. The density of 3.45 g/cm<sup>3</sup> calculated for four formula units in the unit cell agrees with the observed density of 3.4 ± 0.1 g/cm<sup>3</sup>. The OsNCl<sub>5</sub><sup>2-</sup> ion is required crystallographically to possess *m* symmetry. The coordination about the Os atom is distorted octahedral. The Cl atoms *cis* to the nitrido ligand are bent away from the N atom. The Os-N distance is 1.614 (13) Å. The three independent Os-Cl distances *cis* to the N atom do not differ significantly from one another and average 2.362 (2) Å, but the Os-Cl distance *trans* to the N atom is considerably longer at 2.605 (4) Å. This contradicts the results from a previously reported structure of K<sub>2</sub>OsNCl<sub>5</sub> in which the *trans* Os-Cl distance was reported to be much shorter than the *cis* distances. The results on a number of compounds with metal-nitrogen multiple bonding are intercompared and trends are rationalized in terms of nonbonded interactions.

### Introduction

This is the fifth paper in a series that describes structural studies of compounds that contain metal-nitrogen multiple bonding. In previous papers the structures of five compounds of Re(V) have been reported: ReNCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>,<sup>1</sup> ReNCl<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>,<sup>2</sup> ReCl<sub>3</sub>(NC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>,<sup>3</sup> ReCl<sub>3</sub>(NC<sub>6</sub>H<sub>4</sub>COCH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>,<sup>3</sup> and ReCl<sub>3</sub>(NCH<sub>3</sub>)(P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>.<sup>4</sup> The Re-N bond lengths in the latter four complexes are reasonably consistent with current theory; *i.e.*, the formal triple bond in the five-coordinate

nitrido compound ReNCl<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>, 1.602 (9) Å, is shorter than the formal Re-N double bonds in the arylimino complexes ReCl<sub>3</sub>(NC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 1.709 (4) Å, ReCl<sub>3</sub>(NC<sub>6</sub>H<sub>4</sub>COCH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 1.690 (5) Å, and ReCl<sub>3</sub>(NCH<sub>3</sub>)(P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, 1.685 (11) Å. In the six-coordinate nitrido complex ReNCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> the situation is different. The formal Re-N triple bond in this compound is 1.788 (11) Å, almost 0.2 Å longer than that in the related five-coordinate compound, and almost 0.1 Å longer than the formal double bonds in the arylimino complexes. Moreover, the Re-Cl bond which is *trans* to the N atom in this compound is considerably longer at 2.563 (4) Å than the Re-Cl bond *cis* to the N atom, 2.454 (4) Å. In the arylimino complexes the Re-Cl bond length

(1) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(2) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

(3) D. Bright and J. A. Ibers, *ibid.*, **7**, 1099 (1968).

(4) D. Bright and J. A. Ibers, *ibid.*, **8**, 703 (1969).

*cis* to the N atom is within 0.02 Å of the Re–Cl distance *trans* to the N atom.

Very little structural information is available on analogous compounds. The inclusive list of compounds studied (apart from those mentioned above) appears to be:  $\text{VCl}_3(\text{NCl})$ ,<sup>5</sup>  $\text{KOsO}_3\text{N}$ ,<sup>6</sup>  $\text{K}_2\text{OsNCl}_5$ ,<sup>7</sup> and  $\text{K}(\text{OsNBr}_4(\text{H}_2\text{O})) \cdot \text{H}_2\text{O}$ .<sup>7</sup> In  $\text{VCl}_3(\text{NCl})$  the V–N distance is 1.642 (9) Å. Allowing 0.06 Å for the difference in covalent radii of V and Re,<sup>8</sup> this formal double-bond distance is in good agreement with our results on the arylimino complexes. In  $\text{KOsO}_3\text{N}$  the tetrahedral anion is disordered such that O cannot be distinguished from N. The Os–N distance is given as 1.62 Å, but the error in this early determination is probably in excess of 0.1 Å. Similarly, in  $\text{K}_2\text{OsNCl}_5$  and  $\text{K}(\text{OsNBr}_4(\text{H}_2\text{O})) \cdot \text{H}_2\text{O}$  the Os–N distances are reported to be 1.60 Å, but these values are very uncertain as the structures were solved from projection data and were apparently not refined. In addition, a surprising feature of the reported  $\text{K}_2\text{OsNCl}_5$  structure is that the Os–Cl distance *trans* to the nitrido ligand is extremely short, 2.16 Å, while the Os–Cl distances *cis* to the N atom are normal at 2.40 Å. A Os–Cl  $\delta$  bond has been proposed to explain the unusual shortness of the *trans* distance in this compound.<sup>9</sup> Yet the effect is a direct contradiction of the results on  $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$ ,<sup>1</sup> since Re(V) and Os(VI) are isoelectronic.

In order to check that the *trans* Os–Cl value of 2.16 Å was not a typographical error in the paper, we took the structural parameters reported by Atovmyan and Bokii<sup>7</sup> and calculated the interatomic distances for their structure. We found that the reported parameters did indeed correspond to the reported bond lengths, but also that the proposed structure contains a nonbonded  $\text{K} \cdots \text{N}$  ( $\text{K} \cdots \text{OH}_2$  in  $\text{K}(\text{OsNBr}_4(\text{H}_2\text{O})) \cdot \text{H}_2\text{O}$ ) interaction of 1.68 Å. This strongly suggests that the structure reported by Atovmyan and Bokii is incorrect.

The bond lengths in  $\text{K}_2\text{OsNCl}_5$  were of particular interest to us for comparison with our earlier results. Moreover, this compound is of general interest since it has been known for many years<sup>10</sup> and it and its derivatives have been studied in detail by spectroscopic methods.<sup>11,12</sup> Accordingly we decided to redetermine the structure of  $\text{K}_2\text{OsNCl}_5$  to a precision comparable with that obtained in our previous studies on Re(V) complexes, and we report the results of this study here.

### Collection and Reduction of the Intensity Data

A sample of  $\text{K}_2\text{OsNCl}_5$  was prepared by the method of Clifford and Kobayashi,<sup>13</sup> and crystals were grown

(5) J. Strähle and H. Bärnighausen, *Z. Anorg. Allgem. Chem.*, **357**, 325 (1968).

(6) F. M. Jaeger and J. E. Zanstra, *Rec. Trav. Chim.*, **51**, 1013 (1932).

(7) L. O. Atovmyan and G. B. Bokii, *Zh. Strukt. Khim.*, **1**, 501 (1960); *J. Struct. Chem. (U.S.S.R.)*, **1**, 486 (1960).

(8) R. B. Heslop and P. L. Robinson "Inorganic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, p 71.

(9) V. M. Volkov and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **134**, 351 (1960).

(10) A. Werner and K. Dinklage, *Ber.*, **34**, 2698 (1901).

(11) J. Lewis and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **6**, 12 (1958).

(12) W. P. Griffith, *J. Chem. Soc.*, 3694 (1965).

(13) A. F. Clifford and C. S. Kobayashi, *Inorg. Syn.*, **6**, 204 (1960).

by the slow evaporation of dilute hydrochloric acid solutions. Preliminary X-ray photographs showed that the diffraction symmetry of the crystals is mmm.

The cell constants and their standard deviations were determined from a least-squares refinement<sup>1</sup> of the setting angles of 13 reflections that had been carefully centered on a Picker automatic four-circle diffractometer at 22° using Mo  $K\alpha_1$  radiation ( $\lambda$  0.70930 Å). The results are:  $a = 13.27$  (2) Å,  $b = 9.85$  (1) Å,  $c = 6.84$  (1) Å. The systematic absences observed on Weissenberg and precession photographs are:  $0kl$  for  $k + l$  odd and  $hk0$  for  $h$  odd. These extinctions are consistent with either of the space groups  $D_{2h}^{16}$ -Pnma or  $C_{2v}^9$ -Pn2<sub>1</sub>a.

The calculated density of the compound, assuming four  $\text{K}_2\text{OsNCl}_5$  units per cell, is 3.45 g/cm<sup>3</sup>. This is consistent with the density  $3.4 \pm 0.1$  g/cm<sup>3</sup> obtained by pycnometry using diiodomethane as the immersion medium.

From these data, if the space group is Pnma, then the  $\text{OsNCl}_5^{2-}$  ion is required crystallographically to possess m symmetry. If the space group is Pn2<sub>1</sub>a, no symmetry need be imposed on the ion.

The above results are not in agreement with those of Atovmyan and Bokii,<sup>7</sup> who reported an orthorhombic cell with dimensions  $a = 8.92$  Å,  $b = 12.91$  Å,  $c = 7.24$  Å, and space group Cmc2<sub>1</sub> with  $Z = 4$  for this compound. This is surprising as Atovmyan and Bokii's cell is in excellent agreement with the one found by Verhulst in an early X-ray investigation of  $\text{K}_2\text{OsNCl}_5$ .<sup>14</sup> To check that we had indeed prepared  $\text{K}_2\text{OsNCl}_5$ , an elemental analysis was carried out on our sample. *Anal.* Calcd for  $\text{K}_2\text{OsNCl}_5$ : K, 17.01; Os, 41.37; Cl, 38.57; N, 3.05. Found: K, 17.68; Os, 40.87; Cl, 39.17; N, 3.07. This, coupled with the fact that the infrared spectrum of our sample was the same as that reported by Lewis and Wilkinson,<sup>11</sup> convinced us that our sample was genuine  $\text{K}_2\text{OsNCl}_5$  and the structural analysis was continued. Possible reasons for the discrepancies in the unit cells and space groups reported for this compound are discussed later.

A crystal of approximate dimensions 0.1 × 0.1 × 0.3 mm was selected, and in preparation for an absorption correction, the crystal was carefully measured using a micrometer eyepiece and the indices of the crystal faces were determined with the aid of an optical goniometer. The orthorhombic forms developed were identified as {011} and {201}.

The crystal was mounted on the diffractometer with the  $b^*$  axis (the longest dimension of the crystal) direction within 5° of the  $\phi$  axis. The crystal was deliberately set so that no symmetry axis coincided with the  $\phi$  axis in an attempt to minimize multiple diffraction effects.<sup>15</sup> Data were collected and processed in a manner similar to that previously described.<sup>1,2</sup>

The data were collected using Mo  $K\alpha$  radiation; the diffracted beams were filtered through 3 mils of Zr foil. The intensities were measured by the  $\theta$ -2 $\theta$  scan technique at a takeoff angle of 1.1°. At this angle the

(14) J. Verhulst, *Bull. Soc. Chim. Belges*, **42**, 359 (1932).

(15) W. H. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

intensity of a reflection was about 80% of its maximum value as a function of takeoff angle. The scan range in  $2\theta$  was  $-0.6^\circ$  from the Mo  $K\alpha_1$  peak ( $\lambda$  0.70930 Å) to  $+0.6^\circ$  from the Mo  $K\alpha_2$  peak ( $\lambda$  0.71359 Å). Stationary crystal-stationary counter background counts of 10 sec were taken at each end of the scan, and the scan rate was  $1^\circ/\text{min}$ . The Picker system automatically inserts copper foil attenuators into the diffracted beam if its intensity exceeds about 7000 counts/sec during the scan. The thicknesses of the attenuators were chosen to give attenuation factors of approximately 2.5. Thus errors due to coincidence losses were minimized.

As a check on the stability of both the crystal and the electronic equipment, four reflections were measured every 12 hr throughout the data collection period. These reflections showed no significant change in intensity during this time. Data were collected from the  $hkl$  planes only, out to  $\theta(\text{Mo } K\alpha_1) \leq 25^\circ$ . At higher  $\theta$  values very few reflections had significant intensity. A total of 843 independent reflections were measured.

After initial correction for background, the standard deviation,  $\sigma(I)$ , of the corrected intensity  $I$  was estimated from the formula

$$\sigma(I) = [\text{CT} + 0.25(t_o/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count obtained in time  $t_o$ ,  $B_1$  and  $B_2$  are the background counts, each obtained in time  $t_b$ , and  $I = \text{CT} - 0.5(t_o/t_b)(B_1 + B_2)$ . The value of  $p$  was initially taken to be 0.05. The intensities were next corrected for Lorentz and polarization factors and then for absorption. The calculated absorption coefficient for this compound is  $174.7 \text{ cm}^{-1}$  with Mo  $K\alpha_1$  radiation. The calculated transmission factors ranged from 0.27 to 0.34.<sup>16</sup> Of the 843 reflections measured, 156 were found to have  $I < 3\sigma(I)$ . These reflections will be referred to as being below background.

### Solution and Refinement of the Structure

In the least-squares refinements the function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes, respectively, and  $w = 4F_o^2/\sigma^2(F_o^2)$ . The agreement factors are defined as  $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$  and  $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ .

The scattering factors used in computing the contributions to the structure amplitudes from N, Cl, and  $K^+$  were those tabulated by Ibers,<sup>17</sup> and those for Os were calculated by Cromer and Waber.<sup>18</sup> The effects

of anomalous scattering<sup>19</sup> were included in the structure factor calculations; the values of  $\Delta f'$  and  $\Delta f''$  for Os, Cl, and  $K^+$  were those listed by Cromer.<sup>20</sup> The scattering factors for  $K^+$  are preferred to those for the neutral atom since the potassium atoms in the structure are isolated from the other atoms and the cationic charge is therefore localized. In the  $\text{OsNCl}_5^{2-}$  anion, however, the charge is probably not localized, but may be spread over all of the atoms that make up the anion. Thus the charge on the anion was neglected. Only the 687 reflections with intensities above background were used in the refinements.

The coordinates of the osmium atom were readily determined from the three-dimensional Patterson function. A cycle of least-squares refinement (after which the values of  $R_1$  and  $R_2$  were 32.5 and 38.8%) followed by a difference Fourier synthesis served to locate the potassium and chlorine atoms. The positions of the K and Cl atoms strongly suggested that the space group is Pnma rather than Pn2<sub>1</sub>a, and in accordance with this the former space group was assumed for the remainder of the analysis.

The position of the N atom was determined in a subsequent difference Fourier synthesis, and a further cycle of least-squares refinement with all atoms constrained to vibrate isotropically gave agreement factors  $R_1 = 4.5\%$  and  $R_2 = 5.6\%$ . In the next cycle all atoms were allowed to vibrate anisotropically. This gave  $R_1 = 3.3\%$  and  $R_2 = 4.2\%$ , a highly significant improvement over the isotropic model.

The data were now inspected and it was found that for the strong, low-order reflections  $|F_o|$  was consistently less than  $|F_c|$ . This suggested that the data were subject to extinction effects. Accordingly, Zachariasen's extinction parameter<sup>21</sup> was refined<sup>22</sup> as a parameter in the next least-squares cycle. The agreement factors were  $R_1 = 3.3\%$  and  $R_2 = 4.1\%$ .

The principal magnitudes and directions of the thermal motions of the atoms were next evaluated. These values show no anomalies. In particular, the atoms (Cl<sub>1</sub>, Cl<sub>2</sub>, Cl<sub>3</sub>, and N) that lie in the mirror plane (if the space group is Pnma) show no excessive thermal motion normal to this plane, and in fact the directions of maximum vibration of all four atoms lie in the plane. This strongly suggests that the mirror plane is genuine and that the space group is truly the centrosymmetric one, Pnma. Supporting this conclusion is our failure to observe a piezoelectric effect and also the agreement between the observed and calculated structure factors, which is about as good as can be expected with our present techniques. Thus no attempt was made to refine the structure in the noncentrosymmetric space group Pn2<sub>1</sub>a.

At this stage of refinement the standard deviation of an observation of unit weight was 1.29. This is suffi-

(16) The computer programs used in this work were PICK and PICKOUT, for generating and processing the data, NUCLS, the Northwestern University least-squares refinement program which, in its nongroup form, closely resembles the Busing-Levy ORFLS program, and local modifications of Zalkin's FORDAP Fourier summation program, Hamilton's GONO absorption correction program, the Busing-Levy ORFFE function and error program, and Johnson's ORTEP thermal ellipsoid plotting program.

(17) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(18) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(19) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(20) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(21) W. H. Zachariasen, *ibid.*, **23**, 558 (1967).

(22) R. G. Delaplane and J. A. Ibers, *ibid.*, in press.

TABLE I  
 FINAL PARAMETERS FOR  $\text{K}_2\text{OsNCl}_5$ 

Atom	$x$	$y$	$z$	$\beta_{11}^a$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Os	0.09285 (3) <sup>b</sup>	1/4	0.18969 (7)	0.00287 (4)	0.00428 (7)	0.01014 (14)	0	0.00042 (5)	0
N	-0.0016 (9)	1/4	0.0211 (19)	0.0051 (8)	0.0037 (10)	0.0209 (32)	0	0.00019 (14)	0
Cl <sub>1</sub>	0.24791 (24)	1/4	0.40342 (48)	0.00329 (17)	0.00704 (33)	0.01103 (58)	0	-0.00135 (27)	0
Cl <sub>2</sub>	-0.00025 (24)	1/4	0.46498 (49)	0.00364 (19)	0.00797 (34)	0.01383 (78)	0	0.00276 (31)	0
Cl <sub>3</sub>	0.21955 (27)	1/4	-0.07233 (44)	0.00426 (19)	0.00696 (33)	0.01064 (65)	0	0.00104 (31)	0
Cl <sub>4</sub>	0.10586 (19)	0.01128 (23)	0.19054 (35)	0.00445 (16)	0.00473 (23)	0.01685 (51)	-0.00009 (13)	-0.00043 (24)	-0.00035 (26)
K	0.35453 (18)	0.00086 (24)	0.18968 (36)	0.00460 (16)	0.00845 (25)	0.01760 (51)	0.00011 (14)	0.00144 (23)	0.00005 (30)

<sup>a</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(\beta_{11}h + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>b</sup> Numbers in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digits.

ciently close to the theoretical value of 1.00 to suggest that our method for estimating  $\sigma(I)$  is a reasonable one. However, a good test of the validity of a weighting scheme in a least-squares refinement procedure is that the contribution to the function being minimized,  $\Sigma w(|F_o| - |F_c|)^2$ , be equal for various classes of observations, for example, those based on the magnitudes of  $|F_o|$  and on the  $(\sin \theta)/\lambda$  values. An examination of the data showed that this was not the case and that the strong, low-order reflections were the major contributors to the least-squares residual. Among the causes of this may be (1) systematic errors introduced by our assumption of neutral scatterers in the  $\text{OsNCl}_5^{2-}$  ion and (2) the failure of some of the assumptions made in calculating the extinction correction, namely, that the crystal is spherical in shape and that the absorption and mosaicity are isotropic.

In a final round of calculations the values of  $\sigma(I)$  were rederived for a value of  $p = 0.06$  and were then multiplied by  $[1 + [q/((\sin \theta)/\lambda)^2]]^{1/2}$  where  $q$  is an arbitrary constant. The value of  $q$  was chosen as 0.06 since using this value the contributions to  $\Sigma w(|F_o| - |F_c|)^2$  were reasonably constant for all classes of reflections.

A cycle of least-squares refinement using this new weighting scheme gave  $R_1 = 3.3\%$  and  $R_2 = 3.9\%$ . The estimated standard deviation of an observation of unit weight was now 1.01, and the distribution of  $\Sigma w(|F_o| - |F_c|)^2$  was still reasonably constant throughout all ranges of  $|F_o|$  and  $(\sin \theta)/\lambda$ . No parameter changed by more than one estimated standard deviation during this cycle. The final value of the variable extinction parameter, on an absolute scale, is  $6.7 (1) \times 10^{-7}$ .

The final least-squares parameters, together with their standard deviations as derived from the inverse matrix, are given in Table I. Table II lists the final values of  $|F_o|$  and  $|F_c|$  (in electrons  $\times 10$ ).

### Results

The parameters of Table I, together with the unit cell translations and symmetry operations of space group  $\text{Pnma}$ , lead to a structure that consists of layers of  $\text{OsNCl}_5^{2-}$  ions that alternate with layers of  $\text{K}^+$  ions along the  $b$  axis. The ions are well separated; the shortest distance from a  $\text{K}^+$  ion to any other atom in the structure is  $3.19 \text{ \AA}$  (to  $\text{Cl}_3$ ). A stereoscopic pair of views of the contents of a unit cell is given in Figure 1.

Figure 2 shows the  $\text{OsNCl}_5^{2-}$  ion labeled with bond distances. A more complete set of interatomic distances in the structure is given in Table III and the bond angles in the  $\text{OsNCl}_5^{2-}$  ion are listed in Table IV.

The root-mean-square amplitudes of vibration of the various atoms are listed in Table V. The directions of these principal vibrations can be discerned, at least approximately, from the figures. As is usually found, the relative values of the bond lengths are independent of the assumptions made about the thermal motion of the atoms. The most reasonable vibration model for this structure is that the nitrogen and chlorine atoms ride on the osmium atom. Corrections applied to the bond lengths using this model<sup>23</sup> lead to increases of no more than twice the appropriate estimated standard deviations.

The  $\text{OsNCl}_5^{2-}$  ion possesses almost exact  $C_{4v}$  symmetry. The Cl-Os-N angle is not significantly different from linearity at  $178.8 (5)^\circ$ , and the Cl<sub>2</sub>-Os-Cl<sub>4</sub> and Cl<sub>3</sub>-Os-Cl<sub>4</sub> angles are very close to  $90^\circ$  at  $89.24 (6)$  and  $89.44 (6)^\circ$ , respectively. The anion is, however, distorted from an ideal octahedral configuration by a movement of the chlorine atoms *cis* to N away from the nitrogen atom such that the angles Cl<sub>2</sub>-Os-Cl<sub>3</sub> and Cl<sub>4</sub>-Os-Cl<sub>4'</sub> are  $166.0 (1)$  and  $169.1 (1)^\circ$ , respectively. Distortion of a similar nature was also found in  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ ,<sup>3</sup>  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ ,<sup>3</sup> and  $\text{ReOCl}_3(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ .<sup>24</sup> The reasons for these distortions will be discussed in the next section.

The three independent Os-Cl distances *cis* to the nitrogen atom do not differ significantly from one another and average  $2.362 (2) \text{ \AA}$ . This value is in excellent agreement with the results frequently reported for the third-row transition metal-chlorine distances in relatively simple six-coordinate compounds (*e.g.*,  $2.36 \text{ \AA}$  in  $\text{OsCl}_6^{2-}$ ,<sup>25</sup>  $2.35 \text{ \AA}$  in  $\text{ReCl}_6^{2-}$ ,<sup>26</sup> and  $2.38 \text{ \AA}$  in  $\text{OsO}_2\text{Cl}_4^{2-}$ ,<sup>27</sup>). It is interesting that these distances are much shorter than the corresponding distances in  $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$ ,<sup>1</sup>  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ ,<sup>3</sup>  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{COCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ ,<sup>3</sup> and  $\text{ReCl}_3(\text{NCH}_3)(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2$ ,<sup>4</sup> the other six-coordinate compounds with metal-nitrogen multiple

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TABLE V  
ROOT-MEANS-SQUARE AMPLITUDES OF VIBRATION (Å)  
FOR  $K_2OsNCl_5$

Atom	Min	Intermed	Max
Os	0.145 (1)	0.151 (1)	0.164 (1)
N	0.134 (18)	0.213 (17)	0.223 (18)
Cl <sub>1</sub>	0.146 (5)	0.185 (5)	0.186 (4)
Cl <sub>2</sub>	0.141 (6)	0.198 (4)	0.213 (5)
Cl <sub>3</sub>	0.154 (5)	0.185 (4)	0.199 (5)
Cl <sub>4</sub>	0.152 (4)	0.195 (4)	0.204 (4)
K	0.186 (3)	0.204 (3)	0.219 (3)

in  $Re_3Cl_{12}^{3-}$ <sup>28</sup> and  $Re_3Cl_{11}^{2-}$ <sup>29</sup> and the length of these bonds has been attributed to steric effects. It is, however, unusual to find distances of this order in octahedral complexes. As far as we are aware there is only one reported example of a bond of comparable length in an octahedral complex and that is the Re-Cl distance of 2.56 Å which is similarly *trans* to the nitrido ligand in  $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$ .<sup>1</sup> We shall show in the following section that in common with the trinuclear species the extreme lengths of these bonds can also be attributed to steric forces.

The Os-N distance in  $OsNCl_5^{2-}$  is 1.614 (13) Å. This value is in good agreement with the distances found in the  $OsO_3N^-$  ion, 1.62 Å,<sup>6</sup> and in  $ReNCl_2(P(C_6H_5)_3)_2$ ,<sup>2</sup> 1.602 (9) Å, but is very much shorter than the Re-N distance 1.79 (1) Å found in  $ReNCl_3(P(C_2H_5)_2C_6H_5)_3$ .<sup>1</sup>

### Discussion

**Atovmyan and Bokii's Structures.**—The crystal structure of  $K_2OsNCl_5$  reported here is completely unrelated to the structure reported previously for this compound by Atovmyan and Bokii.<sup>7</sup> However, the dimensions of the  $OsNCl_5^{2-}$  ion reported by Atovmyan and Bokii do agree in some respects with the results reported here. Specifically, the Os-N and Os-Cl(*cis*) distances of 1.60 and 2.40 Å reported by Atovmyan and Bokii are in reasonable agreement with our findings of 1.614 (13) and 2.362 (2) Å for these distances. The two structures are definitely not in agreement on the Os-Cl(*trans*) distances. Whereas Atovmyan and Bokii reported an unusually short distance of 2.16 Å, we, on the other hand, found this distance to be unusually long at 2.605 (4) Å.

One statement in Atovmyan and Bokii's paper may give a clue to the reason for this discrepancy in the structures. They reported great difficulty in growing crystals of  $K_2OsNCl_5$  that were suitable for X-ray study. We experienced no difficulty in growing crystals of this compound, provided that the HCl concentration of the mother liquor was high enough to prevent hydrolysis of the anion. The long Os-Cl bond *trans* to the nitrido ligand is consistent with a chlorine atom that is extremely labile and highly susceptible to

replacement by  $H_2O$  in a solution where the concentration of  $Cl^-$  ion is low. Our attempts to grow crystals using pure water as the solvent resulted in formation of brown precipitates if the solution was evaporated slowly or production of small, poorly formed red crystals that were unsuitable for X-ray examination if the solution was evaporated rapidly. Unfortunately, neither Atovmyan and Bokii nor Verhulst<sup>14</sup> (who found the same unit cell and space group as Atovmyan and Bokii in an early X-ray investigation of  $K_2OsNCl_5$ ) gave details of crystallization techniques. However, if the crystallization was carried out from pure water, it would not be surprising if crystals of  $K(OsNCl_4(H_2O)) \cdot H_2O$  were actually isolated. This view is supported by the report<sup>7</sup> that  $K_2OsNCl_5$  is isostructural with  $K(OsNBr_4(H_2O)) \cdot H_2O$ , a fairly well-characterized compound.<sup>30</sup> Nevertheless, this still does not explain the existence of impossible nonbonded distances ( $K \cdots N = 1.68$  Å,  $O \cdots N = 1.68$  Å) in their structures of  $K_2OsNCl_5$  and  $K(OsNBr_4(H_2O)) \cdot H_2O$ , respectively.

**The Bonding in Metal-Nitrogen Compounds.**—A listing of the distances between adjacent atoms in the five six-coordinate complexes studied so far in this series of papers is drawn up in Table VI. The points to note in this table are (1) that excluding the distance in  $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$  of 3.26 Å, the  $Cl \cdots N$  distances are reasonably constant at about 3.02 Å for the remaining compounds, (2) that the  $Cl \cdots Cl$  distances are very similar for all five compounds at around 3.33 Å, and (3) that the nonbonded distances involving  $P \cdots Cl$ , but not  $P \cdots N$ , vary over a relatively large range. An inspection of the molecular models shows that there is a definite correlation between the nonbonded  $P \cdots$  ligand distances and the orientation of the phosphine group with respect to this ligand. The shorter  $P \cdots$  ligand distances occur when, on looking down the metal-phosphorus bond, the ligand appears between the P-R bonds of the  $PR_3$  group (R = alkyl or aryl), and the longest distances occur when the ligand appears obscured by a P-R bond. Thus, when considering the nonbonded  $P \cdots$  ligand distances the ligand  $\cdots R$  distances must also be taken into account. ( $P \cdots$  ligand distances with the corresponding ligand  $\cdots R$  distances are given in Table VII.) Taking this into account the nonbonded distances of all five compounds are very similar and we suggest that the stereochemical configurations are largely determined by intramolecular packing. We can now present a unified view of the bonding in these complexes. We assume that the overriding feature in these compounds is the metal-nitrogen bond, which is by far the strongest bond in each complex.

The  $OsNCl_5^{2-}$  ion (A) can then be imagined to be built up as follows. The Os-N distance is 1.61 Å and the Os-Cl distances *cis* to the N atom are 2.36 Å. These distances in a system with N-Os-Cl angles of 90° lead to short  $N \cdots Cl$  interactions of 2.8 Å, and to

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TABLE VI

	DISTANCES BETWEEN ADJACENT ATOMS IN (A)				
	A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>	D <sup>a</sup>	E <sup>a</sup>
M <sup>a</sup> -N	1.61 <sup>d</sup>	1.79	1.71	1.69	1.69
M-Cl( <i>trans</i> ) <sup>b</sup>	2.61	2.56	2.43	2.41	2.41
M-Cl( <i>cis</i> )	2.37	2.45	2.42	2.40	2.41
	2.36			2.43	2.43
	2.36				
M-P <sup>c</sup>	...	2.44	2.47	2.46	2.48
		2.47		2.46	2.49
		2.49			
N...Cl( <i>cis</i> )	3.03	3.26	3.04	3.11	3.11
	3.00			2.98	2.94
	2.98				
Cl( <i>cis</i> )...Cl( <i>cis</i> )	3.32	...	...	...	...
	3.32				
Cl( <i>cis</i> )...Cl( <i>trans</i> )	3.32	3.37	3.34	3.30	3.34
	3.27			3.28	3.28
	3.35				
N...P	...	3.11	3.15	3.02	3.12
		3.16		3.15	3.12
		3.02			
P...Cl( <i>cis</i> )	...	3.35	3.48	3.36	3.42
		3.35	3.42	3.42	3.30
			3.56	3.47	
			3.41	3.63	
P...Cl( <i>trans</i> )	...	3.55	3.28	3.32	3.26
		3.25		3.32	3.37
		3.58			

<sup>a</sup> M is the metal atom. <sup>b</sup> *cis* and *trans* in the table show positions relative to the nitrogen atom. <sup>c</sup> All P atoms are *cis*. <sup>d</sup> Approximate estimated standard deviations of these figures are: M-N, Cl...Cl, and P...Cl, 0.01 Å; N-Cl and N-P, 0.02 Å; M-P and M-Cl, 0.005 Å. <sup>e</sup> Results are from this work. <sup>f</sup> See ref. 1. <sup>g</sup> See ref. 3. <sup>h</sup> See ref. 4.

relieve this, the Cl atoms are bent away from the N atom until the N...Cl distances are at the optimum value, about 3.0 Å. In this configuration the Cl(*cis*)...Cl(*cis*) distances are also close to their optimum value, 3.33 Å. This bending away of the *cis* Cl atoms also forces out the *trans* Cl atom so that the Os-Cl(*trans*) distance is 2.61 Å when the nonbonded Cl(*cis*)...Cl(*trans*) distances are all normal.

In the rhenium imino complexes (C, D, E) the Re-N distance of 1.7 Å is longer than the corresponding distance in OsNCl<sub>5</sub><sup>2-</sup>, but the ligands *cis* to the N atom are much more crowded as two chlorines have been replaced by two phosphine groups. Thus, although it would appear that the optimum N...(*cis* ligand) interactions could be achieved by bending away the *cis* ligands in the same manner as in the osmium complex, this is not so since it would result in even closer packing of the *cis* ligands. The answer is to lengthen the Re-(*cis* ligand) bonds as well as bend the ligands away from the nitrogen. This extension of the *cis* bonds makes it possible for the *trans* chlorine atom to approach much closer to the metal atom than was possible in the osmium compound, and a Re-Cl(*trans*) distance com-

TABLE VII

NONBONDED P...Cl DISTANCES vs. NONBONDED Cl...R DISTANCES

P...Cl	Cl...R		
	Min	Intermed	Max
3.25	3.30	3.91	5.25
3.26	3.37	3.89	5.00
3.28	3.31	4.11	4.95
3.30	3.58	3.59	5.09
3.32	3.43	4.08	5.00
3.32	3.50	4.05	5.00
3.35	3.24	4.17	5.05
3.35	3.35	4.17	5.01
3.36	3.53	3.91	5.09
3.37	3.32	4.33	4.95
3.41	3.53	4.00	5.14
3.42	3.36	4.58	4.89
3.42	3.50	4.06	5.11
3.42	3.64	3.90	5.18
3.47	3.30	4.73	4.90
3.48	3.39	4.77	4.87
3.55	3.52	4.93	4.93
3.56	3.48	4.79	4.96
3.58	3.47	4.93	4.97
3.63	3.70	4.88	4.93

parable with the Re-Cl(*cis*) distances is found in these complexes.

The case of ReNCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (B) is rather more complex than the two considered above. The plane *cis* to the nitrogen atom now contains three phosphine groups and is therefore highly overcrowded. To relieve the overcrowding the bonds must lengthen still more than in the imino complexes, and the *cis* chlorine atom and the phosphine group *trans* to it are pushed out of the basal plane of the octahedron away from the nitrogen atom. The *trans* chlorine is therefore pushed away from the metal atom, and again a "trans effect" is observed. The Re-N distance, 1.79 Å, is very long in this compound. Hitherto we have regarded the metal-nitrogen bond length as inviolable (although clearly this is not so, and we must expect some lengthening due to steric strain in all of these systems). However, it is an open question as to whether or not the final configuration with the phosphines at the optimum distance from the nitrogen occurs because the nature of the metal-nitrogen bonding makes the distance 1.79 Å and the phosphines move into their final positions to reduce strain between them or whether the nitrogen moves to 1.79 Å from the rhenium because the phosphines force it there. If the former conditions are true, then we have already proposed a scheme involving antibonding between the metal and the nitrogen that accounts for the long distance.<sup>3</sup> However, in view of the success of the present simple steric approach in predicting the distances observed in OsNCl<sub>5</sub><sup>2-</sup> and the imino complexes, it seems that the latter case is much more likely. That this distance is long because of steric effects was originally suggested in the paper describing the structure of this compound.<sup>1</sup>

This idea that the bond lengths are determined mainly by steric factors has much to commend it.

We account for the finding of generally longer bonds as the number of phosphine groups in the molecule increases and the absence of any structural *trans* effect in the imino complexes, as well as the finding of structural *trans* effect in both nitrido complexes. In addition, the failure to isolate a triphenylphosphine analog of  $\text{ReNCl}_2(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_5\text{H}_5)_3$  may be rationalized. Incorporation of three bulky triphenylphosphine groups into the molecule sets up such steric strain that one of these groups is expelled and a five-coordinate species  $\text{ReNCl}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$  is obtained. Both the five-coordinate and the six-coordinate nitrido compounds have been prepared with diphenylethylphosphine, and in

view of the above results a structural study of the six-coordinate compound should be extremely interesting as an example of an overcrowded molecule. We can now also rationalize the apparent insensitivity of the Re-N bond length in the imino complexes to change of the substituent on the nitrogen atom. The Re-N bond is already highly strained so that small changes in the bond strength are dissipated in increasing or relieving the strain in the other ligands.

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## The Crystal and Molecular Structure of Racemic Bis( $\pi$ -azulene)iron

By MELVYN R. CHURCHILL AND JOHN WORMALD

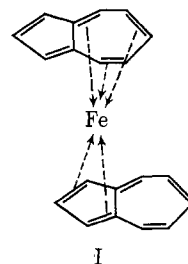
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Bis( $\pi$ -azulene)iron,  $(\text{C}_{10}\text{H}_8)_2\text{Fe}$ , crystallizes in the centrosymmetric monoclinic space group  $\text{P}2_1/c$  ( $\text{C}_{2h}^5$  no. 14) with  $a = 7.523$  (5) Å,  $b = 12.071$  (4) Å,  $c = 15.419$  (16) Å,  $\beta = 98.26$  (4)°,  $Z = 4$ . Observed and calculated densities are  $1.45 \pm 0.03$  and  $1.496$  g cm $^{-3}$ , respectively. A single-crystal X-ray diffraction study has been completed. Data to  $\sin \theta = 0.38$  (Mo  $\text{K}\alpha$  radiation) were collected with a  $0.01^\circ$ -incrementing Buerger automated diffractometer, and the structure was solved using conventional Patterson, Fourier, and least-squares refinement techniques. All atoms have been located, the final discrepancy index being  $R_F = 7.95\%$  for the 1162 independent nonzero reflections. The crystal consists of distinct molecular units of  $(\text{C}_{10}\text{H}_8)_2\text{Fe}$ , separated by normal van der Waals distances. The molecule is found to be a highly substituted ferrocene in which two azulene systems have dimerized *via ortho-para* (i.e., 4-*endo*,6'-*endo*) coupling.

### Introduction

Our recent series of structural studies on the azulene-metal-carbonyl complexes  $\text{C}_{10}\text{H}_8\text{Fe}_2(\text{CO})_5$ ,<sup>1</sup>  $\text{C}_{10}\text{H}_8\text{Mo}_2(\text{CO})_6$ ,<sup>2</sup>  $[(i\text{-C}_3\text{H}_7)(\text{CH}_3)_2\text{C}_{10}\text{H}_5]\text{Mo}_2(\text{CO})_6$ ,<sup>2a,3</sup>  $\text{C}_{10}\text{H}_8\text{Mn}_2(\text{CO})_6$ ,<sup>4</sup>  $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{CH}_3]_2$ ,<sup>5</sup>  $[(\text{CH}_3)_3\text{C}_{10}\text{H}_5]\text{Ru}_4(\text{CO})_9$ ,<sup>6</sup> and  $(\text{C}_{10}\text{H}_8)_2\text{Fe}_4(\text{CO})_{10}$ <sup>7</sup> has indicated that a dominant feature of the azulene-to-metal bonding in these complexes is the utilization of the five-membered ring in a  $\pi$ -cyclopentadienyl $\rightarrow$ metal linkage. The only other presently known class of azulene-metal complexes has as its sole representative<sup>8</sup> the compound bis( $\pi$ -azulene)iron.<sup>9</sup> On the basis of its proton magnetic

resonance spectrum and hydrogenation studies (the complex takes up 5 mol of hydrogen), this species has been represented as a complex stabilized by metal-diene and metal-triene bonding (as in I).<sup>9</sup>



We have therefore undertaken an X-ray structural analysis of bis( $\pi$ -azulene)iron, with a view to determining unequivocally its molecular structure. A brief report of this work has appeared previously.<sup>10</sup>

### Experimental Section

Bis( $\pi$ -azulene)iron was prepared *via* the "tris(isopropyl)iron" method,<sup>11</sup> following the procedure of Fischer and Müller.<sup>9</sup> Anhydrous  $\text{FeCl}_3$  (1.3 g) and azulene (2 g) in dry diethyl ether (35 ml) were treated at  $-50^\circ$  under  $\text{N}_2$  with isopropylmagnesium bromide,

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