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The Crystal and Molecular Structure of Dinitrogenpentaammineosmium(II) Chloride, $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$, and Related Ruthenium Complexes

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The crystal and molecular structure of the dinitrogen complex dinitrogenpentaammineosmium(II) chloride, $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2$, has been solved using the intensities of 708 independent X-ray reflections measured with a scintillation counter. Crystals are orthorhombic, of space group $Pnma$; $a = 13.575$ (4), $b = 10.465$ (2), $c = 6.873$ (2) Å; $Z = 4$; $d_o = 2.56 \pm 0.03$, $d_o = 2.54$ g cm⁻³. Full-matrix least-squares refinements have led to a conventional R factor of 3.9%. The structure is ordered with osmium atoms at the center of a distorted, octahedral coordination environment consisting of six nitrogen atoms, five from ammonia ligands and one from a dinitrogen ligand. The osmium-ammonia N bonds range from 2.12 to 2.15 Å and the osmium-dinitrogen bond is 1.84 Å while the dinitrogen NN bond is 1.12 Å. The OsNN angle is 179°. Solid solutions of the two compounds $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ have been obtained which are isomorphous to $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$. The frequency of the stretching vibration of the coordinated dinitrogen in the solid solutions is lowered. This is explained in terms of the structure of $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$.

Earlier structure analyses of dinitrogen complexes have been affected by problems of disorder,^{1,2} complexity,³ and instability.⁴ In the ordered structures, metal-dinitrogen bond lengths are short as is characteristic of multiple bonding, while the dinitrogen (N≡N) bond is little changed from its length in gaseous dinitrogen.⁴ The metal-N≡N bond angles have all been observed to be close to 180°.

The compound $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2$ was chosen for the present study because of its molecular simplicity and its X-ray powder photographs indicated that it was probably isomorphous with $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ for which the structure has been reported.⁵ In the latter structure, the central ruthenium ion is at the center of an ordered octahedral arrangement of one chlorine and five ammonia ligands, with three of the ammonia groups and the ruthenium and coordinated chlorine atoms lying on crystallographic mirror planes.

Chemically, the osmium-dinitrogen complex is interesting because of the stability of the OsN_2 entity and the relatively low energy of the $\nu(\text{N}\equiv\text{N})$ absorption together with the high energy of the $\nu(\text{Os}-\text{N}_2)$ absorption in its infrared spectrum.

The crystal structure of the osmium-dinitrogen complex is also of interest as we have found that the analogous ruthenium complex $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ forms solid solutions with $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ where the orthorhombic crystal symmetry of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ takes precedence over cubic $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$.

Experimental Section

Preparation of Dinitrogenpentaammineosmium(II) Chloride.—The dinitrogen complex $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ was prepared as a pale yellow microcrystalline solid by prolonged boiling of $[\text{Os}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ or $(\text{NH}_4)_2\text{OsCl}_6$ in hydrazine hydrate. *Anal.* Calcd for $\text{Cl}_2\text{H}_{16}\text{N}_7\text{Os}$: N, 26.1. Found: N, 25.9. Recrystallization of this complex proved difficult. Allen and Stevens⁶ reported that the complex is stable in aqueous solution and in concentrated hydrochloric acid; hence recrystallization was attempted from both water and dilute hydrochloric acid. In water, the complex

was found to decompose to give brown sludges after several days at room temperature, although at lower temperatures (*ca.* 5°) this did not occur. In dilute hydrochloric acid (0.1 *M*) slow decomposition to pale yellow $[\text{Os}(\text{NH}_3)_5\text{Cl}]\text{Cl}$ occurs.

A crystalline product was finally obtained by slow cooling, from about 80°, of a saturated hydrazine hydrate solution of $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$. Microscopic and photographic examination of approximately octahedral crystals indicated that very few were suitable for X-ray intensity work. The fragment used was cut from a larger crystal in this batch.

Crystallographic Data.—Preliminary precession photographs revealed orthorhombic symmetry and all recorded spectra satisfied the conditions $hkl0$, $h = 2n$; $0kl$, $k + l = 2n$. These conditions are consistent with the space group $Pnma$ (centrosymmetric) or a nonstandard setting of $Pna2_1$ (noncentrosymmetric). This analysis has confirmed the centrosymmetric space group as the correct one.

The crystal was mounted rigidly, but in a random orientation, on a glass fiber for data collection using a Hilger and Watts four-circle automatic diffractometer. All diffractometer experiments were carried out using zirconium-filtered Mo $K\alpha$ radiation, for which the mean $K\alpha$ wavelength was taken as 0.7107 Å. A takeoff angle of 3° was used and the circular receiving apertures were positioned 23 cm from the crystal.

The setting angles of twelve reflections, accurately centered in a 1.5-mm diameter aperture, were used for a least-squares refinement⁷ of the cell parameters and crystal orientation matrix. The cell parameters, with standard deviations, for the orthorhombic space group $Pnma$ were found to be $a = 13.575$ (4), $b = 10.465$ (2), $c = 6.873$ (2) Å (25°). The density of the bulk sample was obtained using a calibrated density gradient tube (bromoform-1,2-dibromomethane) and found to lie in the range 2.56 ± 0.03 g cm⁻³. For four molecules in the unit cell the calculated density is 2.54 g cm⁻³. The mosaicity of the crystal was examined by means of open-counter ω scans. The width, at half-peak height, for a typical strong low-angle reflection was 0.20°.

The intensity data were then collected, using an aperture of 5-mm diameter and the θ - 2θ scan technique. A symmetric scan range of 1.60° in 2θ , centered on the calculated peak position, was composed of 80 steps of 0.75-sec duration. Stationary-crystal, stationary-counter background counts of 15 sec were taken at each end of the scan range. Attenuation was not required as the intensity of the diffracted beam did not exceed 5000 counts/sec for any reflection.

Intensities were measured for 2370 reflections in the equivalent reciprocal space octants hkl , $\bar{h}\bar{k}l$, and $\bar{h}kl$ and for which $0 < \theta < 25^\circ$. For the $\bar{h}\bar{k}l$ and $\bar{h}kl$ data, collection was limited to those 768 reflections for which $I > \sigma(I)$ in the first form. The data were corrected for absorption and the equivalent

(1) F. Bottomley and S. C. Nyburg, *Chem. Commun.*, 897 (1966); *Acta Crystallogr., Sect. B*, **24**, 1289 (1968).

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(3) B. R. Davies, N. C. Payne, and J. A. Ibers, *ibid.*, **8**, 2719 (1969); *J. Amer. Chem. Soc.*, **91**, 1240 (1969).

(4) B. R. Davies and J. A. Ibers, *Inorg. Chem.*, **9**, 2768 (1970).

(5) C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 137 (1962).

(6) A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967).

(7) W. R. Busing, International Summer School on Crystallographic Computing, Ottawa, Canada, 1969, Paper 12; W. R. Busing and H. A. Levy, Report ORNL-4054, Oak Ridge National Laboratory, Oak Ridge, Tenn.

TABLE I
 POSITION AND THERMAL PARAMETERS FOR THE STRUCTURE $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2^a$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11} or <i>B</i>	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os	0.10523 (5)	1/4	0.18327 (9)	0.00310 (4)	0.00387 (6)	0.0100 (1)	0.0000	-0.00015 (8)	0.00000
Cl	0.1409 (2)	0.0004 (3)	0.6833 (4)	0.0038 (1)	0.0063 (3)	0.0143 (6)	-0.0003 (2)	-0.0001 (3)	0.0000 (4)
N(1)	0.0043 (1)	1/4	0.0047 (2)	2.4 (2)					
N(2)	-0.056 (1)	1/4	-0.108 (2)	3.6 (3)					
N(3)	0.007 (1)	1/4	0.425 (2)	3.3 (3)					
N(4)	0.222 (1)	1/4	0.395 (2)	3.1 (3)					
N(5)	0.212 (1)	1/4	-0.041 (2)	3.5 (3)					
N(6)	0.1087 (7)	0.045 (1)	0.189 (1)	3.1 (2)					

^a For atoms refined anisotropically, the form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Numbers given in parentheses in this table and in others in this paper are estimated standard deviations in the least significant digits. No numbers are given for parameters whose values are fixed by symmetry.

reflections were averaged.^{8,9} During the data collection, the intensities of three standard reflections were recorded at regular intervals. The crystal showed no signs of decomposition since the intensities of these standards showed only those deviations from the mean predicted by counting statistics.

The linear absorption coefficient for the compound $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ using Mo $K\alpha$ radiation is 143.8 cm^{-1} . The triangular wedge shape of the crystal was characterized by bounding planes (201), (11 $\bar{2}$), (120), ($\bar{2}$ 11), and (2 $\bar{2}$ 1) and appropriate dimensional measurements. Transmission coefficients, calculated using gaussian integration, ranged from 0.5306 for the 430 reflection to 0.2185 for the $\bar{3}$ 11 reflection.⁹ For many equivalent reflections, the intensity of the hkl reflection was significantly different from the intensity of the other two equivalent reflections, before absorption corrections were applied, but agreed well after absorption correction.

After averaging, the 2370 recorded reflections yielded a data set of 912 reflections of which $I \geq 3\sigma(I)$ for 578 reflections, $3\sigma(I) > I \geq 2\sigma(I)$ for 66 reflections, $2\sigma(I) > I \geq \sigma(I)$ for 62 reflections, and $I < \sigma(I)$ for the remaining 206 reflections.

Solution and Refinement of the Structure.—All full-matrix least-squares refinements were carried out on *F*, the function minimized being $\sum w(|F_o| - |F_c|)^2$, where the weight (*w*) is taken as $4F_o^2/\sigma^2(F_o^2)$; $|F_o|$ and $|F_c|$ are the amplitudes of the observed and calculated structure factors. In all calculations of *F_c*, the atomic scattering factors for osmium were taken from Cromer and Waber,¹⁰ those for hydrogen from Stewart, *et al.*,¹¹ and those for other atoms from usual tabulations.¹² The effects of anomalous dispersion from the osmium and chlorine atoms were included in the calculation of *F_c*; the values of $\Delta f'$ and $\Delta f''$ used were those of Cromer.¹³

Initial positional parameters for all nonhydrogen atoms, except those in the dinitrogen ligand, were those given by Prout and Powell⁵ for the corresponding atoms in $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. Using isotropic temperature factors and *hkl* data uncorrected for absorption, the refinement¹⁴ converged to give agreement factors of $R_1 = 10.1\%$ and $R_2 = 12.8\%$, where $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and the weighted *R* factor $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum (|F_o|)^2)^{1/2}$. A difference fourier synthesis¹⁴ revealed four peaks of intensity approximately $6 \text{ e}/\text{\AA}^3$. Two of these were close to the osmium atom and the other two clearly revealed a coordinated dinitrogen ligand. This structure, with anisotropic temperature factors assigned to the osmium and chlorine atoms (whose isotropic temperature factors were relatively high), refined

TABLE II

IDEALIZED POSITIONAL PARAMETERS FOR IN-PLANE AMMONIA HYDROGEN ATOMS

Ammonia group	Hydrogen	<i>x</i>	<i>y</i>	<i>z</i>
N(3)	H(1)	0.051	1/4	0.565
	H(2)	-0.041	0.338	0.420
N(4)	H(1)	0.296	1/4	0.318
	H(2)	0.216	0.338	0.490
N(5)	H(1)	0.289	1/4	0.026
	H(2)	0.204	0.338	-0.134

to give agreement factors of $R_1 = 7.7\%$ and $R_2 = 7.6\%$. After correction for absorption and averaging equivalent reflections, the refinement converged to give agreement factors of $R_1 = 4.0\%$ and $R_2 = 4.5\%$.

Another difference synthesis was calculated and this revealed no peaks of height greater than $1.5 \text{ e}/\text{\AA}^3$. The high electron density was near the ammonia nitrogen atoms. Hydrogen positions for the "in-plane" ammonia groups were calculated for each of the two orientations possible if these groups are ordered. The temperature factors of the hydrogen atoms in the calculated positions were then refined and best agreement was found when the hydrogen atoms were near high peaks in the difference maps. These calculations were taken to indicate definite orientations for the NH_3 groups lying in the crystallographic mirror plane. With all hydrogen atoms fixed in their calculated positions and with anisotropic thermal parameters applied to osmium and chlorine atoms, final refinement of 35 parameters resulted in values of 3.9 and 4.4% for R_1 and R_2 , respectively. The largest coordinate shift in this refinement was 0.01 of its estimated standard deviation. (Refinement with all nonhydrogen atoms anisotropic showed no significant improvement in the agreement factors.) There was no evidence of significant secondary extinction effects.

Average values of the minimized function obtained after the final cycle of refinement showed little dependence on *F_o* or on $\lambda^{-1} \sin \theta$ which indicates that the relative weighting system is reasonable. The error in an observation of unit weight was 0.613. A final difference map still shows peaks of up to $1.4 \text{ e}/\text{\AA}^3$ near the hydrogen atom positions, but in the remainder of the map, peaks do not rise above $1.0 \text{ e}/\text{\AA}^3$.

Final positional and thermal parameters are shown in Table I along with estimated standard deviations obtained from the final cycle of the least-squares refinement. The idealized positional parameters ($\text{N-H} = 1.13 \text{ \AA}$, $\text{Os-N-H} = 109^\circ 58'$) for the hydrogen atoms are listed in Table II. The final values of $|F_o|$ and $|F_c|$ (in electrons) are given (Table III¹⁵) for the 706 reflections used in the final refinement. For the 206 reflections omitted from the refinement none had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. These data are not included in Table III.

Preparation of Solid Solutions of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.—The two salts $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were dissolved in 0.05 *M* hydrochloric acid to give a nearly saturated solution at room temperature. The solution was then evaporated over concentrated sulfuric acid and solid sodium hydroxide desiccants under reduced pressure. The crystalline

(8) Calculations were carried out at the University of Canterbury using an IBM 360/44 computer with 32K words of core storage and twin 2315 disk drives.

(9) The data processing program HLGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens). Numerical absorption corrections were applied using program DABS which is a modified version of DATAPH (P. Coppens). Mathematical methods are fully described in "Crystallographic Computing," Munksgaard, Copenhagen, 1970.

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

(11) R. F. Stewart, D. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(12) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1958.

(13) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(14) Structure factor calculations and least-squares refinements were carried out using program CVCLS and Fourier summations using program FOURIER. These are highly modified versions of the well-known programs ORFLS (W. R. BUSING, K. O. MARTIN, and H. A. LEVY) and FORDAP (A. ZALKIN), respectively. Molecular dimensions and their esd's were obtained from program ORFFE also by Busing, Martin, and Levy.

(15) Table III will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1662. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE IV

Compd or solid soln	Sym	a, Å	b, Å	c, Å	Cell vol, Å ³	$\nu(\text{NN})$, cm ⁻¹	$\nu(\text{M-N}_2)$, cm ⁻¹
[Ru(NH ₃) ₅ Cl]Cl ₂	<i>Pnma</i>	13.465 (4)	10.542 (5)	6.802 (3)	965.5
25% [Ru(NH ₃) ₅ N ₂]Cl ₂	<i>Pnma</i>	13.485 (3)	10.537 (3)	6.811 (2)	967.8	2065	Not obsd
75% [Ru(NH ₃) ₅ Cl]Cl ₂							
56% [Ru(NH ₃) ₅ N ₂]Cl ₂	<i>Pnma</i>	13.56 (1)	10.520 (8)	6.835 (8)	975.1	2078	508
44% [Ru(NH ₃) ₅ Cl]Cl ₂							
[Ru(NH ₃) ₅ N ₂]Cl ₂	<i>Fm3m</i> <i>F432</i> <i>F43m</i>	10.141 ^a	10.141 ^a	10.141 ^a	1042.9 ^a	2112	510
90% [Ru(NH ₃) ₅ N ₂]Cl ₂	<i>Cmcm</i>	10.337 (7)	9.260 (8)	10.46 (1)	1000.9	2105	495
10% [Ru(NH ₃) ₅ Cl]Cl ₂							
50% [Ru(NH ₃) ₅ N ₂]Cl ₂	<i>Cmcm</i>	10.349 (3)	9.366 (7)	10.373 (8)	1005.4	2093	501
50% [Ru(NH ₃) ₅ CO]Cl ₂							
10% [Ru(NH ₃) ₅ N ₂]Cl ₂	<i>Cmcm</i>	10.381 (4)	9.271 (4)	10.44 (1)	1004.4	2093	501
90% [Ru(NH ₃) ₅ CO]Cl ₂							
[Os(NH ₃) ₅ N ₂]Cl ₂	<i>Pnma</i>	13.575 (4)	10.465 (2)	6.873 (2)	976.4	2025, 2010	536

^a From ref 1.

product formed after the volume had been reduced by about one-fifth was collected. Different crops of crystals from the one solution varied only slightly in composition. The compositions of the products were determined from the measurement of evolved dinitrogen after treatment of the crystals with ceric ions and also from spectrophotometric measurement of the intensity of the absorption at 221 nm (ϵ 16,000) characteristic of the dinitrogen complex. The composition of the solid solutions (as mole per cent) is given in Table IV.

The [Ru(NH₃)₅N₂]Cl₂-[Ru(NH₃)₅Cl]Cl₂ solid solutions were also prepared by dissolving the dinitrogen complex in hydrochloric acid and allowing the solution to stand until crystals formed. Some of the dinitrogen complex was oxidized under these conditions with loss of dinitrogen and the ruthenium-pentaammine-chloro complex was formed. After some time the two complexes in solution crystallized as a solid solution.

Preparation of Dinitrogenpentaammineruthenium(II) Chloride.—The complex was prepared according to method 3 of Allen, *et al.*¹⁶ *Anal.* Calcd for Cl₂H₁₅N₇Ru: N (NH₃), 24.6. Found: N (NH₃), 24.5.

Preparation of Pentaamminechlororuthenium(III) Chloride.—The complex [Ru(NH₃)₅Cl]Cl₂ (3 g in 20 ml of water) (prepared by the method of Lever and Powell^{17a}) was treated with bromine,^{17b} using bromine water in a slight excess rather than bromine vapor. The addition of bromine was accompanied by the initial yellow solution becoming paler and then turning orange as excess bromine accumulated. At this point concentrated hydrochloric acid was added to give a 1:1 mixture, and the solution was heated under reflux for 2 hr (excess bromine was allowed to escape). The product [Ru(NH₃)₅Cl]Cl₂ was formed as yellow-orange crystals which were collected and recrystallized from 0.1 M hydrochloric acid. *Anal.* Calcd for Cl₂H₁₅N₅Ru: N, 23.9. Found: N, 24.0.

Measurement of Cell Parameters of Solid Solutions.—Cell dimensions were obtained from powder diffraction data recorded on a Philips PW1010/30 automatic recording goniometer using Cu K α radiation ($\lambda(\text{Cu K}\alpha_1)$ 1.54051 Å, $\lambda(\text{Cu K}\alpha_2)$ 1.54433 Å). The goniometer was calibrated using sodium chloride with a cell constant of 5.6391 Å.¹⁸ Calculations of unit cell dimensions were by conventional nonlinear least-squares methods.¹⁹

Infrared Measurements.—The infrared spectra were recorded on both a Shimadzu IR 27G spectrophotometer and a Perkin-Elmer 337 spectrophotometer. The measurements are accurate to ± 5 cm⁻¹.

Results

Description of the Structure of [Os(NH₃)₅N₂]Cl₂.—The structure consists of discrete [Os(NH₃)₅N₂]²⁺ units situated so that the osmium atom, three ammonia groups, and the two atoms of the dinitrogen group lie

(16) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

(17) (a) F. M. Lever and A. R. Powell, *J. Chem. Soc.*, 1477 (1969); (b) A. D. Allen, T. Eliades, R. O. Harris, and V. P. Reinsalu, *Can. J. Chem.*, **47**, 1605 (1969).

(18) G. Ericsson, *Struct. Rept.*, **18**, 574 (1954).

(19) Program POWDER was used, adapted for the IBM 360/44 computer.

TABLE V
SELECTED BOND LENGTHS AND ANGLES
IN THE COMPLEX [Os(NH₃)₅N₂]Cl₂

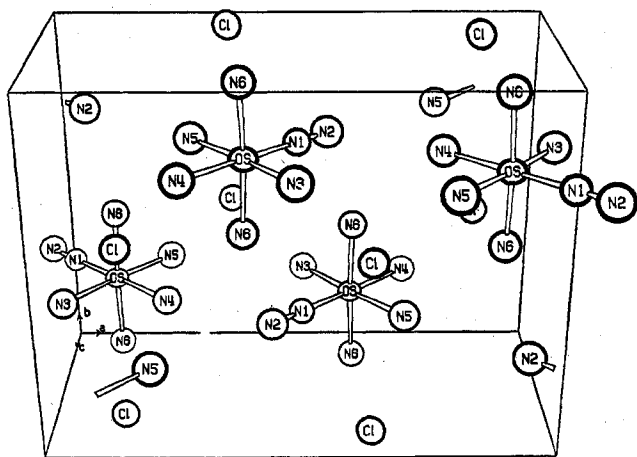
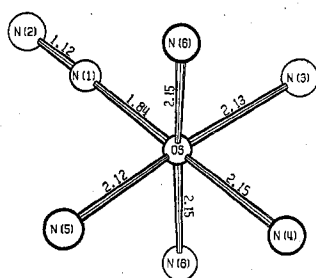
Bond Lengths, Å			
OsN(1)	1.842 (13)	OsN(5)	2.119 (16)
OsN(3)	2.126 (15)	OsN(6)	2.145 (10)
OsN(4)	2.151 (15)	N(1)N(2)	1.12 (2)
Bond Angles in the Cation [Os(NH ₃) ₅ N ₂] ²⁺ , Deg			
N(2)N(1)Os	178.3 (1.3)	N(3)OsN(5)	175.3 (0.6)
N(1)OsN(3)	93.3 (0.6)	N(3)OsN(6)- (N(6)')	90.0 (0.2)
N(1)OsN(4)	179.4 (0.5)	N(4)OsN(5)	89.2 (0.6)
N(1)OsN(5)	91.4 (0.6)	N(4)OsN(6)- (N(6)')	88.4 (0.3)
N(1)OsN(6)- (N(6)')	91.6 (0.3)	N(5)OsN(6)- (N(6)')	89.9 (0.2)
N(3)OsN(4)	86.1 (0.6)	N(6)OsN(6)'	176.7 (0.5)
Distances from the Chloride Ion, Å			
ClN(3)	3.39 (1)	ClN(6)	3.43 (1)
ClN(4)	3.46 (1)	ClN(6)	3.46 (1)
ClN(4)	3.53 (1)	ClN(6)	3.54 (1)
ClN(5)	3.37 (1)	ClN(6)	3.53 (1)

^a N(6) and N(6)' are two N(6) nitrogen atoms related by the mirror plane through the cation.

on a crystallographic mirror plane. The remaining two coordinated ammonia groups are situated on each side of this plane, almost directly above and below the osmium atom. The four ammonia ligands cis to the dinitrogen group are bent slightly away (*ca.* 2°) from it and toward the trans ammonia ligand, but the displacement is too small to be statistically significant.

The closest nonbonded contacts of the chloride anion are given in Table V. Consideration of these distances in conjunction with the hydrogen atom coordinates, given in Table II, suggests significant hydrogen bonding may occur between Cl and N(3) and N(5). Typical N...Cl distances involving H bonding are in the region of 3.26–3.4 Å.²⁰ A view of the unit cell is given in Figure 1 and the coordination of the cation is depicted in Figure 2. This figure also shows the numbering system used for the cation nitrogen atoms. A selection of interatomic bond lengths and angles is presented in Table V together with the estimated standard deviations. The root-mean-square amplitudes of vibration along the principal axes of thermal motion are given in Table VI for the osmium and chlorine atoms. The directions of the principal axes

(20) K. Sakurai and Y. Tomiie, *Acta Crystallogr.*, **5**, 293 (1952).

Figure 1.—Unit cell contents for the structure of $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$.Figure 2.—Structure and bond lengths for the cation $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$.

can be discerned, at least approximately, from the figures.

The Solid Solutions.—The range of solid solutions, the space group, and cell dimensions of each phase and the $\nu(\text{NN})$ and $\nu(\text{Ru}-\text{N}_2)$ infrared stretching frequencies for each phase are given in Table IV. Two types of solid solution formed from the components $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. For compositions up to 56% $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ the solid solution has the space group symmetry $Pnma$ characteristic of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. For higher (90%) percentages of the dinitrogen complex the crystal form is still orthorhombic but the space group is $Cmcm$ and in addition some pure cubic $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ also crystallizes out.

TABLE VI

Atom	ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)		
	Min	Intermed	Max
Os	0.1471 (11)	0.1542 (11)	0.1704 (11)
Cl	0.181 (4)	0.185 (4)	0.194 (4)

Solid solutions of the complexes $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_5\text{CO}]\text{Cl}_2$ were also prepared and these all crystallized in the orthorhombic system with the space group $Cmcm$, which is characteristic of the carbonyl complex.

Discussion

The solution of the crystal and molecular structure of $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ in which all nonhydrogen atoms other than those of the dinitrogen ligand are within experimental error of the reported positions of the corresponding atoms in $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ suggests that the latter structure⁹ was determined correctly. The

solution of the ruthenium complex was obtained from 550 reflections using films. The high R factor of 16.7% was tentatively ascribed to structural disorder but this does not seem reasonable in view of this accurate analysis of the osmium-dinitrogen complex. The possibility of an impurity being the reason has been mentioned.²¹

For the structure $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ the important bond lengths and bond angles are those involving the dinitrogen group, especially the short Os-N(1) bond length of 1.84 Å.

(a) **The Dinitrogen (NN) Bond Length.**—The dinitrogen (N≡N) bond length (1.12 (2) Å) is only slightly longer than that observed for gaseous dinitrogen (1.0976 (2) Å²²), and it is similar to that observed in other relevant structures which range from 1.106 Å for $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ to 1.124 Å for the dimeric complex $[\text{Ru}_2(\text{NH}_3)_{10}\text{N}_2](\text{BF}_4)_4$.^{3,23}

The slight increase in the dinitrogen (NN) bond length on complex formation is not surprising, especially as the $\nu(\text{NN})$ absorption frequency is lowered by 320 cm^{-1} , from the value for free dinitrogen, in the complex $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$. The small change in bond length and large change in infrared stretching frequency are not unreasonable in view of the nature of the variation of force constant with bond length.²⁴

(b) **The Osmium-Dinitrogen Bond Length.**—The short metal-dinitrogen bond length of 1.84 (1) Å is indicative of multiple bonding. This feature of dinitrogen complexes has already been commented on.³ The Os-N(1) bond length is similar to the metal-carbon bond length in carbonyls and the metal-nitrogen bond length in nitrosyls.^{25,26}

The structure of a monocarbonylpentaammine complex has not yet been determined, but the structure of the ruthenium(II) complex $[\text{Ru}(\text{NH}_3)_5\text{NO}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ has been reported. In this structure the Ru-NO bond length²⁸ of 1.80 (2) Å is similar to that observed for the osmium-dinitrogen bond length.

The osmium-dinitrogen bond length of 1.84 Å may also be compared with bond lengths of other osmium-nitrogen bonds. The bond length is less than the average single-bond distance of 2.14 Å observed for the Os-NH₃ bond but it is longer than the Os≡N triple bond of 1.61 Å²⁷ observed in $\text{K}_2[\text{OsNCl}_5]$. Ruthenium and rhenium M=N double bonds⁴ are about 1.70 Å; hence it would appear that the Os-N₂ bond is probably intermediate in character between a single and a double bond.

(c) **The Osmium-Ammonia Bond Lengths.**—The ammonia ligand trans to the dinitrogen is bonded to the osmium with a slightly longer bond than the other ammonia ligands in the xy plane. However, we do not consider this significant especially as the osmium-ammonia N(6) bond is the same length as the osmium-ammonia N(4) bond. This observation is in contrast to what is found for the complex $[\text{Ru}(\text{NH}_3)_5\text{NO}]$ -

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$\text{Cl}_3 \cdot \text{H}_2\text{O}^{26}$ where the ammonia-osmium bond trans to the nitric oxide ligand is significantly longer than the rest.

The difference between the Os-N(NH₃) and Os-N(1) bond lengths of around 0.3 Å is significant and indicative of different bonding for the two types of nitrogen atoms. The Os-NH₃ bond is presumably a single σ bond whereas the short Os-N(1) bond involves a $\text{Os}_{d_{z^2}} \rightarrow \text{N}_{2p_{\pi}} \pi$ component.

Solid Solutions.—The formation of the solid solutions is of interest especially as the structure of cubic $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ is modified in the presence of the orthorhombic pentaammine-chloro or -carbonyl complexes, even at high concentrations of the dinitrogen complex. The modification of the structure is reflected in significant changes in the infrared stretching frequency of the coordinated dinitrogen ligand.

The evidence for the crystalline phases being solid solutions is as follows. (a) X-Ray powder photographs of physical mixtures of the two components show lines of both, whereas the solid solutions show lines characteristic only of the orthorhombic component. (b) The dinitrogen complex is not changed chemically in the solid solutions as the species $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ can be recovered from aqueous solutions of the crystalline phases by precipitation as the perchlorate salt. In addition, aqueous solutions of all the solid solutions show the $\nu(\text{NN})$ absorption frequency at 2112 cm^{-1} in the infrared spectrum.

The solid solutions of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ undergo a change in unit cell volume with composition (Table IV), and as the volume decreases, there is a decrease in the stretching frequency of the coordinated dinitrogen.

Since the structures of the two compounds $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ are identical, the $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ component of the solid solution (*Pnma* symmetry) must have the same orientation as does $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ in its crystal lattice.

The unit cell diagram (Figure 1) indicates that the dinitrogen ligand in $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ is orientated toward the N(5) ammonia ligand of a neighboring cation. Hence, in the solid solutions, the dinitrogen and coordinated chloro ligands will also be orientated toward the N(5) ammonia ligand. Therefore it may be expected that as the amount of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ increases in the solid solution, the greater spatial requirement of the dinitrogen ligand, which lies in the

xz plane of the unit cell at $y = 0.25$ and 0.75 , would explain the observed increase in the length of the a and c axes (Table IV). This may be seen by a consideration of interatomic distances. The $\text{Ru}-\text{Cl} \cdots \text{N}(5)$ distance in $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is 6.85 Å whereas the distance $\text{Os}-\text{N} \equiv \text{N} \cdots \text{N}(5)$ is 6.91 Å. Since the $\text{Ru}-\text{N}_2$ bond is longer than the $\text{Os}-\text{N}_2$ bond by at least 0.1 Å, it is clear that the $\text{Ru}-\text{Cl} \cdots \text{N}(5)$ distance is too small to permit ready replacement of Cl with N₂. Hence the unit cell dimensions in the a and c directions increase.

As the concentration of the dinitrogen complex decreases in the solid solutions, the influence of the increasing steric interaction on the dinitrogen bond may push the dinitrogen ligand and ruthenium ion closer together strengthening the metal-N(1) bond and in consequence weakening the N(1)-N(2) bond. This corresponds to a reduction in the $\nu(\text{NN})$ infrared stretching frequency (by as much as 21%).

A recent suggestion²⁸ for the mechanism by which the $\nu(\text{NN})$ infrared stretching frequency in $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{X}_2$ changes with counteranion X is not applicable in this situation. The solid solutions with the *Pnma* space group show a small decrease in unit cell parameter b (Table IV) with increasing percentage of dinitrogen complex. Since the b dimension is controlled by the cation-anion distance, the results suggest that the cation and anion are slightly closer together in the solid solution which contains more of the dinitrogen complex. This situation corresponds to a higher $\nu(\text{NN})$ infrared absorption frequency, whereas the mechanism proposed²⁸ would predict a lower frequency.

This work confirms that bonding between transition metal ions and dinitrogen, like the two isoelectronic ligands CO and NO⁺, is similar and that the bonding involves both σ and π components. The results also suggest that the dinitrogen NN bond is destabilized in the complexes and that the strengths of the dinitrogen and metal-dinitrogen bonds are sensitive to small changes in the lattice environment of the dinitrogen.

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