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The Crystal and Molecular Structure of Potassium Pentachloronitrosylruthenate(II), $K_2[Ru(NO)Cl_5]$

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The structure of potassium pentachloronitrosylruthenate(II), $K_2Ru(NO)Cl_5$, has been refined by least-squares techniques on three-dimensional X-ray data collected by counter methods. The material crystallizes in the space group $P2_12_12_1$ (D_2^4) of the orthorhombic system with four molecules in a cell of dimensions $a = 10{\cdot}363(4)$, $b = 13{\cdot}292(10)$, and $c = 6{\cdot}880(4)$ Å. The observed and calculated densities are 2·70 (2) and 2·729 g.cm^{-3} respectively. Least-squares refinement of the structure has yielded a final value for the conventional R value (on F) of 0·040 for 1347 independent reflections having $F^2 > 3\sigma(F^2)$. The $[Ru(NO)Cl_5]^{2-}$ anion is a slightly distorted octahedron with the Ru–Cl bond length of 2·359(2) Å *trans* to the nitrosyl group shorter than the average *cis* Ru–Cl bond length of 2·372 (8) Å. The Ru–N–O group is approximately linear, with an Ru–N–O bond angle of 176·8 (9)° and Ru–N and N–O bond distances of 1·747 (6) and 1·112 (7) Å, respectively. These values suggest that the nitrosyl group is bonded as NO^+. The coordination around the Ru atom is similar to that found in the isomorphous ammonium salt of this anion.

Introduction

The structure of potassium pentachloronitrosylruthenate(II), $K_2Ru(NO)Cl_5$, has been previously investigated (Khodashova & Bokii, 1960). On the basis of their photographic data, these workers assigned the complex to the space group *Pnma* and reported an unusually long N–O bond length of 1·25 Å. Recently completed structural work on the ammonium salt of this anion (Veal & Hodgson, 1972) gives different values for the bond parameters of the anion, demonstrating a significant shortening of the Ru–Cl bond *trans* to the nitrosyl and a more reasonable N–O bond length of 1·131 (3) Å. Preliminary work in our laboratory suggested that the potassium salt was isomorphous with the ammonium salt and that the correct space group for both was $P2_12_12_1$ rather than *Pnma*.

A detailed infrared study of this complex (Durig, McAllister, Willis & Mercer, 1966) has been reported. These workers conclude from vibrational spectroscopy that in ions of the type $[Ru(NO)X_5]^{2-}$ the Ru–X bond (X= halide) *trans* to the nitrosyl is weaker than the bonds *cis* to the nitrosyl. Recently reported molecular orbital calculations for the complexes $Mn(CO)_5X$ (X= Cl, Br, I), however, have shown (Fenske & DeKock, 1970) that the M–X bond is entirely σ in nature, and that the halogen successfully competes with the carbonyl for σ electron density. Since CO and NO^+ are isoelectronic and Cl^- is a better σ bonder than NO^+, arguments of this type would predict that the Ru–Cl bond *trans* to the NO^+ should be strengthened rather than weakened. The structure of the ammonium salt (Veal & Hodgson, 1972), $(NH_4)_2Ru(NO)Cl_5$, is con-

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sistent with these latter arguments. In order to further test the validity of this hypothesis and insure against any possible hydrogen bonding effects in the ammonium salt, a precise three-dimensional single-crystal X-ray structural determination of the complex $K_2Ru(NO)Cl_5$ was carried out; the results of this investigation are presented here.

Experimental

Potassium pentachloronitrosylruthenate(II) (K & K Labs) was recrystallized from a 2*M* aqueous solution of KCl. A crystal specimen with approximate dimensions $0{\cdot}038 \times 0{\cdot}017 \times 0{\cdot}011$ cm was chosen and coated with shellac to prevent crystal decomposition, since we had observed that decomposition occurs if the material is submitted to prolonged exposure to the atmosphere. The crystal was mounted roughly parallel to the *b* axis, which is approximately parallel to the needle direction of the crystal.

Preliminary examination using precession and Weissenberg photographs suggested that the crystals belong to the orthorhombic system and are isomorphous with the ammonium salt, $(NH_4)_2Ru(NO)Cl_5$ (Veal & Hodgson, 1972). The observed systematic absences are $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd. The $0kl$ reflections with $k+l$ odd and the $hk0$ reflections with h odd appeared to be absent on the photographs, but closer examination of the counter data showed these reflections to be systematically weak but not absent; this strongly suggests that the space group is not *Pnma*, as was reported by Khodashova & Bokii (1960), but is $P2_12_12_1$. The lattice constants obtained by the least-squares procedure described previously (Hodgson, Hale & Hatfield, 1971) are $a=10{\cdot}363$ (4), $b=13{\cdot}292$ (10) and $c=6{\cdot}880$ (4) Å. A density of 2·729 g.cm^{-3} calculated for four formula units in the cell agrees with the value of 2·70 (2) g.cm^{-3} obtained by flotation in diiodomethane/1,2-dibromoethane solution. Hence, no crystallographic symmetry need be imposed on monomeric species in the cell. Intensity data were collected at 24°C with the wavelength assumed as $\lambda(\text{Mo } K\alpha)=0{\cdot}7093$ Å using a Picker four-circle automatic diffractometer as previously described (Meyer, Singh, Hatfield & Hodgson, 1972). A unique data set having $2\theta<60°$ was gathered; a total of 1797 independent intensities was recorded. There were very few data above background at values of $2\theta>60°$. Only one form (hkl) of the data was gathered. Data processing was carried out as previously described (Veal & Hodgson, 1972), the value of p in the expression $\sigma(I)=[c+0{\cdot}25(ts/tb)^2(BH+BL)+(pI)^2]^{1/2}$ being assigned as 0·040.

This term is used to prevent extremely high weight being given to very large reflections (Busing & Levy, 1957).

The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. The absorption coefficient for this compound for Mo $K\alpha$ radiation is 38·015 cm^{-1}. Unfortunately, the coating of shellac on the crystal made it impossible to index the faces of the crystal, and the irregular shape of the sample precluded any acceptable approximation of the identities of the faces; consequently, no absorption correction was applied to the data.

Solution and refinement

All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o|-|F_c|)^2$. In all calculations of F_c the atomic scattering factors for Ru were taken from Cromer & Waber (1965), that for H from Stewart, Davidson & Simpson (1965), and those for Cl and N from Ibers (1962). The effects of anomalous dispersion were included in calculations of F_c (Ibers & Hamilton, 1964), the values of $\Delta f'$ and $\Delta f''$ for Ru, Cl and K being taken from the tabulation of Cromer (1965). The 1347 independent intensities which were greater than three times their estimated standard deviations were used for the refinement of the structure.

Initial values for the atomic coordinates were taken from the ammonium structure (Veal & Hodgson, 1972) with the potassium atoms assigned the positions of the nitrogen atoms. Five cycles of least-squares calculations in which the atoms were assigned variable anisotropic thermal parameters were run; a correction for secondary extinction of the form described by Zachariasen (1963, 1968) was also included. Final values for the usual agreement values, $R_1=\sum |F_o|-|F_c| /\sum|F_o|$ and R_2 (or weighted R value)$=[\sum w(|F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}$ of 0·040 and 0·045 respectively were obtained, and the final value of the extinction coefficient was $2{\cdot}12\ (20)\times 10^{-7}$. Since only one form (hkl) of the data had been collected, two cycles of least-squares refinement were run in which (hkl) was replaced by $(\bar{h}\bar{k}\bar{l})$; this is equivalent to changing the positions (x,y,z) of all the atoms to $(\bar{x},\bar{y},\bar{z})$. As anticipated, since $P2_12_12_1$ is not a polar space group (Ueki, Zalkin & Templeton, 1966; Cruickshank & McDonald 1967) and since the structure is very nearly centrosymmetric (*vide infra*), this change did not cause any significant change in the atomic parameters or in the agreement values R_1 and R_2. No shifts of greater than one standard deviation were observed in any parameter after the last cycle, which was taken as evidence that the refinement had converged.

A difference Fourier synthesis computed at this stage showed no peaks higher than 1·91 e.Å^{-3}, with all peaks larger than 0·80 e.Å^{-3} in the vicinity of the Ru atom; these three relatively large residual peaks suggest that there may be some error in our description of the thermal model of the Ru atom, but are more probably due to our inability to apply an absorption correction to the data. The peak height of the nitrogen atom in this analysis was approximately 12 e.Å^{-3}.

The positional and thermal parameters derived from the last least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Table 1. The observed and calculated structure factors (in electrons) are given in Table 2.

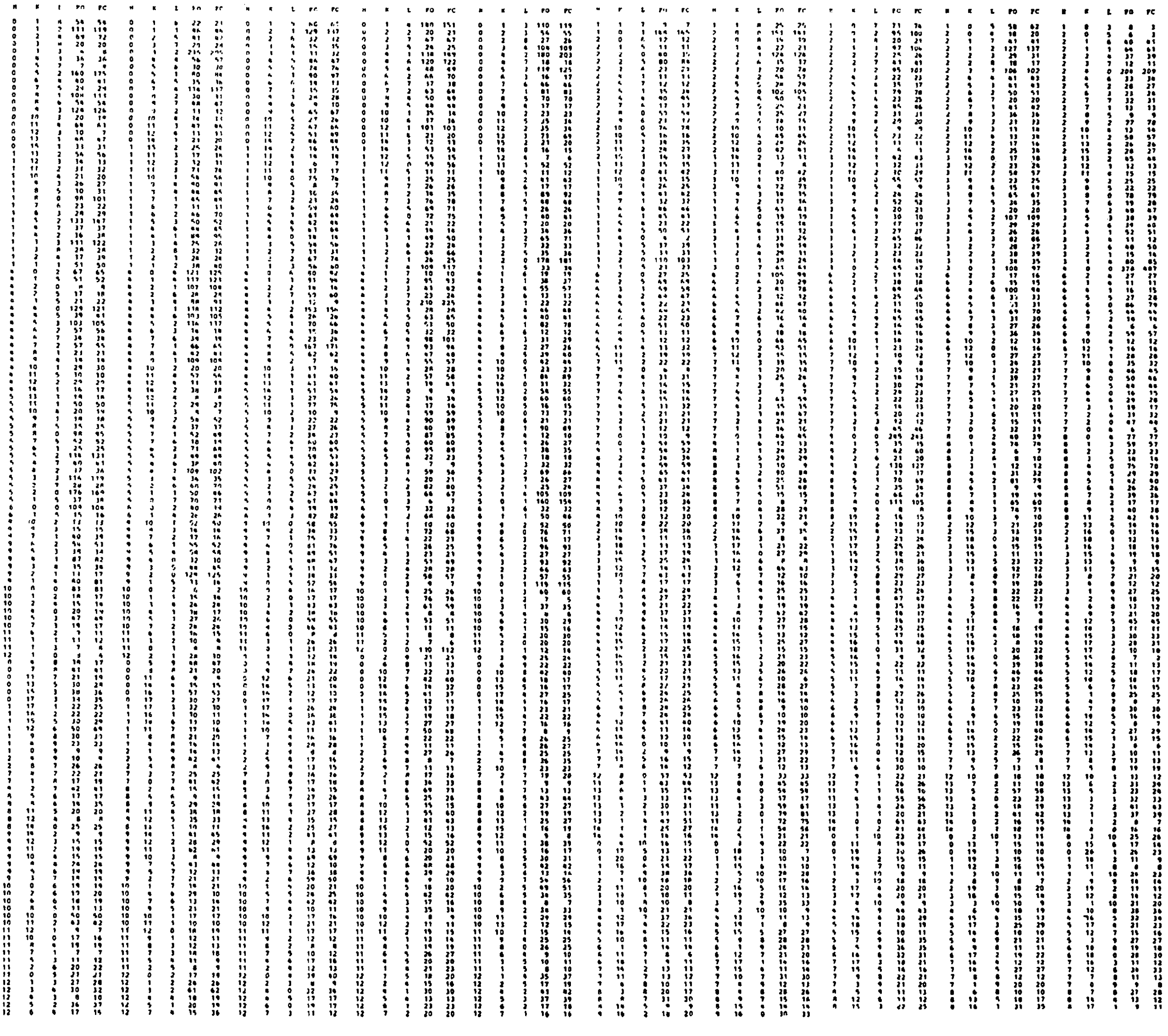
The large standard deviations for the parameters of Cl(1) and Cl(2) are a result of the high correlation between the coordinates of these two atoms. The correla-

Table 1. *Positional and thermal parameters for* $K_2[Ru(NO)Cl_5]$

The form of the anisotropic thermal ellipsoid is $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$. All values are $\times 10^4$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	7 (2)	1417 (1)	1711 (1)	24 (1)	28 (1)	84 (1)	−1 (1)	−1 (1)	3 (1)
N	53 (21)	2412 (4)	55 (7)	15 (6)	32 (2)	109 (8)	2 (8)	−24 (16)	−1 (4)
O	81 (24)	3017 (4)	−1070 (7)	35 (8)	41 (3)	133 (8)	2 (8)	14 (15)	25 (4)
Cl(1)	−2272 (6)	1403 (6)	1816 (12)	26 (3)	51 (3)	206 (14)	−1 (3)	1 (6)	35 (6)
Cl(2)	2298 (6)	1353 (7)	1771 (13)	27 (3)	60 (4)	243 (17)	−2 (3)	2 (6)	20 (7)
Cl(3)	29 (1)	12 (1)	3808 (2)	58 (2)	37 (1)	119 (2)	−3 (5)	−3 (9)	18 (1)
Cl(4)	−16 (11)	2466 (1)	4508 (2)	88 (2)	41 (1)	127 (3)	5 (5)	14 (10)	−21 (1)
Cl(5)	5025 (11)	4736 (1)	918 (2)	91 (2)	42 (1)	106 (3)	−12 (5)	−1 (10)	−16 (1)
K(1)	2498 (6)	3968 (6)	3511 (12)	65 (6)	51 (4)	169 (15)	7 (4)	0 (7)	24 (5)
K(2)	−2510 (6)	3937 (6)	3516 (13)	73 (7)	53 (4)	213 (19)	6 (4)	18 (8)	1 (6)

Table 2. *Observed and calculated structure amplitudes* (*in electrons*) *for* $K_2[RuNOCl_5]$



tion coefficient of the least-squares matrix between the two z coordinates of these atoms, for example, was greater than 0·93, and all of the correlation coefficients between corresponding positional and thermal parameters were greater than 0·90. These high correlations result from the near mirror symmetry at the ruthenium; all atoms in the anion except Cl(1) and Cl(2) lie very near $x=0$, while the coordinates of Cl(2) are approximately related to those of Cl(1) by reflection across the yz plane.

Description of the structure

The structure consists of $[Ru(NO)Cl_5]^{2-}$ anions which are well separated from the potassium cations with no evidence of distortions due to packing effects. The overall geometry is similar to that reported by Khodashova & Bokii (1960), but there are significant differences in the magnitudes of the bond parameters.

The coordination polyhedron about the ruthenium (Fig. 1) is a distorted octahedron with a Ru–N–O linkage which is nearly linear [176·8 (9)°]. The bond parameters for the nitrosyl group are consistent with those of other reported cases of coordinated NO^+, with a Ru–N distance of 1·747 (6) Å and a N–O distance of 1·112 (7) Å. In Table 3 the bond distances and angles found for the anion in this refinement are compared with the values reported by Khodashova & Bokii, and with the values found for the corresponding ammonium salt (Veal & Hodgson, 1972). As can be seen from Table 3, the bond parameters reported here for the potassium salt are similar to those reported for the ammonium salt with the Ru–Cl bond *trans* to the nitrosyl group shorter than the average Ru–Cl bond *cis* to the nitrosyl in both cases. For the potassium salt the Ru–Cl *trans* bond and the average of the *cis* Ru–Cl bonds are 2·359 (2) and 2·372 (8) Å, respectively. Although the range and standard deviations for the *cis* Ru–Cl bonds are much larger for the potassium salt (*vide supra*) than for the ammonium salt, the overall trend is the same in both cases.

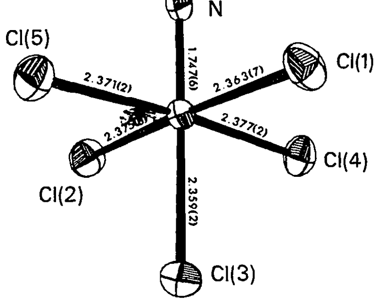


Fig. 1. View of the $[Ru(NO)Cl_5]^{2-}$ ion in $K_2[Ru(NO)Cl_5]$. The thermal ellipsoids are drawn at the 50 % probability level.

Table 3. *Selected intramolecular distances and angles for the* $[Ru(NO)Cl_5]^{2-}$ *anion*

(*a*) Intramolecular distances (Å)

Bond	This work	Khodashova & Bokii*	Ammonium salt†
Ru–Cl(1)	2·363 (7)	2·35	2·374 (2)
Ru–Cl(2)	2·375 (8)	2·34	2·378 (2)
Ru–Cl(3)	2·359 (2)	2·35	2·357 (1)
Ru–Cl(4)	2·377 (2)	2·34	2·378 (1)
Ru–Cl(5)	2·371 (2)	2·35	2·373 (1)
Ru–N	1·747 (6)	1·70	1·738 (2)
N—O	1·112 (7)	1·25	1·131 (3)

(*b*) Intramolecular angles (°)

Angle	This work	Khodashova & Bokii‡	Ammonium salt†
Ru—N—O	176·8 (9)	177·0	176·7 (5)
N—Ru-Cl(1)	93·2 (9)	90·0	91·5 (2)
N—Ru-Cl(2)	90·5 (9)	90·0	91·5 (2)
N—Ru-Cl(3)	176·3 (5)	177·6	178·2 (4)
N—Ru-Cl(4)	94·9 (2)	92·5	94·2 (1)
N—Ru-Cl(5)	89·5 (2)	90·3	91·0 (1)
Cl(5)-Ru-Cl(1)	91·3 (4)	90·0	91·4 (1)
Cl(5)-Ru-Cl(2)	89·2 (4)	90·0	89·0 (1)
Cl(5)-Ru-Cl(3)	87·4 (1)	90·0	87·6 (1)
Cl(5)-Ru-Cl(4)	175·6 (1)	177·2	174·8 (1)
Cl(1)-Ru-Cl(2)	176·3 (1)	180·0	177·0 (1)
Cl(1)-Ru-Cl(3)	88·8 (4)	90·0	88·2 (1)
Cl(1)-Ru-Cl(4)	88·1 (4)	90·0	88·6 (1)
Cl(2)-Ru-Cl(3)	87·5 (4)	87·4	87·3 (1)
Cl(2)-Ru-Cl(4)	91·1 (4)	90·0	90·7 (1)
Cl(3)-Ru-Cl(4)	88·2 (1)	90·0	88·9 (1)

* Khodashova & Bokii (1960).
† Veal & Hodgson (1972).
‡ Values calculated from the positional parameters given by Khodashova & Bokii (1960).

N–O bond

The area of greatest discrepancy between the results of our refinement for this structure and those reported by Khodashova & Bokii (1960) concerns the bond length of the N–O bond. Our value of 1·112 (7) Å is in agreement with the values reported for the N–O bond in the structures of other Ru complexes containing NO^+, *e.g.* 1·16 (2) Å in $[Ru(NO^+)(NO^-)Cl(Ph_3)_2]PF_6$ (Pierpont, VanDerveer, Durland & Eisenberg, 1970), 1·127 (7) Å in $Na_2[Ru(NO)(OH)(NO_2)_4].2H_2O$ (Simonsen & Mueller, 1965), 1·131 (3) Å in $(NH_4)_2Ru(NO)Cl_5$ (Veal & Hodgson, 1972), 1·180 (12) in $RuH(NO)(PPh_3)_3$ (Pierpont, Pucci & Eisenberg, 1971), and 1·197 (13) Å in $[Ru(NO)(diphos)_2]^+$ (Pierpont *et al.*, 1971). The value of 1·25 Å for the N–O reported by the previous workers is clearly not consistent with the distances found in these structures, and is outside of the range for NO^+ in metal nitrosyls (Hodgson & Ibers, 1968).

trans effect

The *trans* effect in complexes containing coordinated NO^+, CO, or N_2 is usually discussed in terms of competition for π-electron density by groups *trans* to each other (Manoharan & Gray, 1966), with the bond to the better π acceptor strengthened relative to the bond *trans* to it. Recently, we postulated a more generalized approach for discussing *trans* effects in six-coordinate systems (Veal & Hodgson, 1972). This approach takes into account both the σ and π nature of the bonds *trans* to each other, with their relative strength dependent on the nature of the bonding in the two ligands and on their ability to compete for σ- and π-electron density. This postulate is based in part on Fenske & DeKock's (1970) molecular orbital calculations on the $Mn(CO)_5L$ (where L=Cl, Br and I) systems, in which they demonstrated that the carbonyl groups *cis* to the halide have slightly stronger σ bonding than the carbonyl group *trans* to the halide although the axial carbonyl has much stronger π bonding character than the equatorial carbonyl groups. Their calculations also suggest that halides are predominately σ-bonding ligands.

The results reported here for $K_2[Ru(NO)Cl_5]$ provide further evidence for the validity of this approach. The $[Ru(NO)Cl_5]^{2-}$ anion is an example in which a σ-bonding ligand, chloride, is *trans* to a predominantly π-bonding ligand which has only weak σ character (NO^+). Our modified approach predicts that the *trans* Ru–Cl bond should be strengthened relative to the *cis* Ru–Cl bonds. The values of 2·359 (2) and 2·372 (8) Å for the *trans* and average *cis* Ru–Cl distances confirm this prediction. We anticipate that further structural data which may become available for complexes of the general type $[M(NO)L_5]$ will also be interpretable in terms of this argument.

In addition to various local programs, the programs for the IBM 370/165 used in this analysis were local modifications of Ibers's *NUCLS* least-squares program, Busing, Levy, and Martin's *ORFFE* function and error program, Zalkin's *FORDAP* Fourier program, and Johnson's *ORTEP* plotting program.

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