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Temperature-Dependence of the Crystal Structure of $K_2[RuCl_5NO]$: A Powder Neutron Diffraction Study

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A powder neutron diffraction study of the crystal structure of $K_2[RuCl_5NO]$ in the electronic groundstate is presented in the temperature range from 25 to 295 K, confirming the orthorhombic space group *Pnma*. Neither a structural nor a magnetic phase transition has been observed. A shortening of the axial Ru–Cl_2 bond occurs with increasing temperature, while the Ru–N bond gets longer. The metal to chloride bonds do not change uniformly.

Introduction

$K_2[RuCl_5NO]$ (potassium pentachloronitroruthenate) can be transformed by light of wavelengths $620 < \lambda < 760$ nm into extremely long-lived ($\tau > 10^7$ s) excited electronic states at temperatures below 200 K (MS_I) and 130 K (MS_{II}), respectively (*1*). This behavior is already known from various nitroprussides ($X[Fe(CN)_5NO] \cdot H_2O$, X = Na_2, Ba, K_2, Pb, Li_2, etc.) (*2*). The structure of sodium nitroprusside has been studied by neutron diffraction for all three states (*3–5*).

The structure of nitroprusside is rather complicated (84 atoms in the unit cell) (*4, 5*), and the changes in the crystal structure between the three states are small. In addition, only part of the molecules can be excited simultaneously. We are therefore looking for compounds with a simpler structure. The electronic excited, metastable states in $K_2[RuCl_5NO]$ are mainly related to variations in the metal–NO bond, similarly to our previous investigations (*3–5*).

As a first study for planned measurements on the crystal structure of the metastable states in $K_2[RuCl_5NO]$, we present here the temperature dependence of the groundstate crystal structure of $K_2[RuCl_5NO]$. We performed powder neutron diffraction investigations at four temperatures in the range from 25 to 295 K. The temperatures of 135 and 200 K have been chosen, as they correspond to the decay temperatures of the two excited states (*1*).

Materials and Methods

A polycrystalline sample of $K_2[RuCl_5NO]$ was enclosed under helium in a cylindrical vanadium container of 10 mm diameter and 50 mm height. All measurements were performed using the double-axis-

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TABLE I

AGREEMENT FACTORS R (IN %) AND GOODNESS OF FIT χ^2 BETWEEN OBSERVED AND CALCULATED NEUTRON INTENSITIES OF $K_2[RuCl_5NO]$, BASED ON SPACE GROUP *Pnma*

T [K]	295	200	135	25
R_I	7.78	6.08	5.46	4.06
R_{wp}	3.89	3.70	3.63	3.66
R_{exp}	2.34	2.31	2.36	2.17
χ^2	2.76	2.55	2.37	2.83

multicounter (DMC) diffractometer (*6*) at the reactor Saphir at PSI/Würenlingen (high resolution mode, λ = 1.7012(1) Å, Ge 311 monochromator, vertically focusing). A closed-cycle helium refrigerator cooled the sample, which was oscillated to reduce preferred orientation problems.

$K_2[RuCl_5NO]$ has a molecular weight of 386.55 g/mole. Single crystals are of dark red to black color and have rhombic shape. The structure of $K_2[RuCl_5NO]$ at room temperature was first determined with X-ray techniques on single crystals by different groups (*7–9*). Their results are not consistent. Khodashova and Bokii (*7*) claimed the symmetry to correspond to space group *Pnma* (lattice constants a = 13.31(1) Å, b = 10.25(1) Å, c = 6.84(1) Å). In a reexamination of their data they later published certain minor changes of bondlengths (*8*). Veal and Hodgson (*9*) found some weak reflections forbidden in *Pnma*, lowering the symmetry to space group $P2_12_12_1$ (a = 10.363(2) Å, b = 13.292(3) Å, c = 6.880(1) Å).

As most of the bondlengths determined by the two groups coincide within standard deviations, and as we did not observe the "forbidden" reflections with neutron diffraction performed on perfect single crystals, we determined the symmetry to be

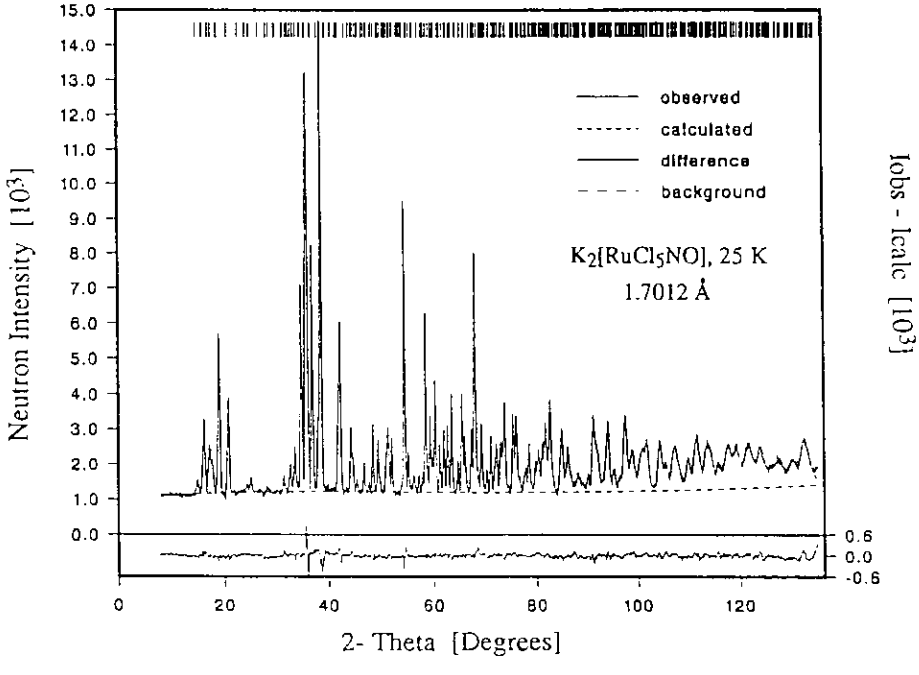

FIG. 1. Observed, calculated, and difference neutron diffraction patterns of $K_2[RuCl_5NO]$ at 25 K, measured with λ = 1.7012(1) Å.

TABLE II

TEMPERATURE DEPENDENCIES OF UNIT CELL PARAMETERS OF $K_2[RuCl_5NO]$

T [K]	a [Å]	b [Å]	c [Å]
25	13.0937(6)	10.3175(4)	6.8389(3)
135	13.1806(7)	10.3393(5)	6.8582(3)
200	13.2258(8)	10.3523(5)	6.8697(4)
295	13.3024(10)	10.3766(6)	6.8920(4)

Note. The errors due to the wavelength uncertainty of 0.01% are not included (λ = 1.7012(1) Å).

Pnma in agreement with (*7*, *8*). Moreover, we did not observe any violation of this space group symmetry in our neutron powder diffraction patterns.

Results

All powder diffraction patterns were refined by means of a modified version of the Wiles and Young program (*10*), including a fit of the background by a polynomial of sixth order. The patterns were corrected for absorption as measured by transmission ($\mu \cdot r$ = 0.311). The peak shape chosen was Gaussian with a correction for asymmetry (as described in (*10*)) for $2\Theta < 45°$, caused by the large active detector height of 90 mm. In order not to introduce too many parameters all atoms were refined with isotropic temperature factors. Despite the oscillation of the sample during the measurement, we had to introduce a preferred orientation parameter along the [100] direction enhancing the goodness of fit by 50%. The low final R factors summarized in Table I (for all measurements) and the 25 K neutron diffraction pattern shown in Fig. 1 demonstrate the good quality of the sample and of the refinement based on the space group *Pnma*. The refined lattice parameters are summarized in Table II, and the positional parameters are given for T = 25 K in Table III. In the temperature range from 25 to 295 K the latter change within about three standard deviations. Detailed lists of all corresponding parameter values for the investigated temperatures are contained in (*5*) and may be obtained on request from the authors.

Neither a structural nor a magnetic phase transition has been observed between 295 and 25 K. Without any modification of the model (*7*, *8*) all the relevant parameters, such as lattice parameters, isotropic temperature factors, fractional coordinates, and

TABLE III

STRUCTURAL PARAMETERS AND ISOTROPIC DEBYE–WALLER FACTORS (B_{iso}) OF $K_2[RuCl_5NO]$ FOR T = 25 K, REFINED FROM NEUTRON POWDER DATA

Atom	Position	x	y	z	B_{iso} [Å^2]
Ru	4c	1065(5)	2500	1668(7)	0.26(10)
N	4c	0064(4)	2500	0050(6)	0.60(8)
O	4c	−0544(6)	2500	−1124(9)	0.91(14)
Cl_1	4c	0017(5)	2500	4569(5)	0.74(9)
Cl_2	4c	2524(4)	2500	3787(6)	0.52(10)
Cl_3	4c	2233(3)	2500	−0977(5)	0.52(9)
Cl_4	8d	1114(2)	0203(3)	1802(4)	0.57(6)
K	8d	1445(6)	−0003(10)	6481(9)	0.80(15)

Note. Fractional coordinates are in units of [10^{-4}]. All sites are fully occupied.

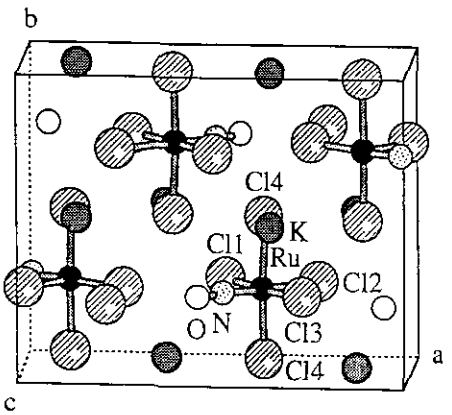

FIG. 2. Unit cell of $K_2[RuCl_5NO]$ corresponding to space group *Pnma*, for $T = 25$ K.

bondlengths, changed continuously with temperature (see Tables II and IV as well as Fig. 3).

Similarly to sodium nitroprusside, the temperature variations of the lattice constants are anisotropic. The change of the *a*-axis is larger (1.6%) than the changes found for the *b*- (0.8%) and *c*-axis (0.6%) (see Table II). The volume of the unit cell shrinks linearly by approximately 2.9% between 295 and 25 K. Surprisingly there was no saturation of the unit cell volume found at low temperatures.

Figure 2 illustrates the unit cell of the $K_2[RuCl_5NO]$ at 25 K.

Figure 3 shows the temperature dependencies of the isotropic temperature factors, indicating a standard behavior. One should mention that the temperature factors of the chlorine atoms appear to be high. We therefore expect an additional libration, as seems reasonable for this molecule. The axial chlorine atom (Cl_2) varies less than the other chlorine atoms. This implies an increasing rotation around the Cl_2–Ru–N–O axis with increasing temperature.

There is no general trend for the temperature behavior of the different bond lengths. The Ru–N bond becomes larger with increasing temperature while the axial Ru–Cl_2 and the N–O bonds decrease. In Table IV the most important bond lengths and bond angles are listed as function of temperature for the $[RuCl_5NO]^{2-}$ molecule in $K_2[RuCl_5NO]$. The same behavior as mentioned above has been observed for the first excited state MS_1 in sodium nitroprusside (*3*, *5*).

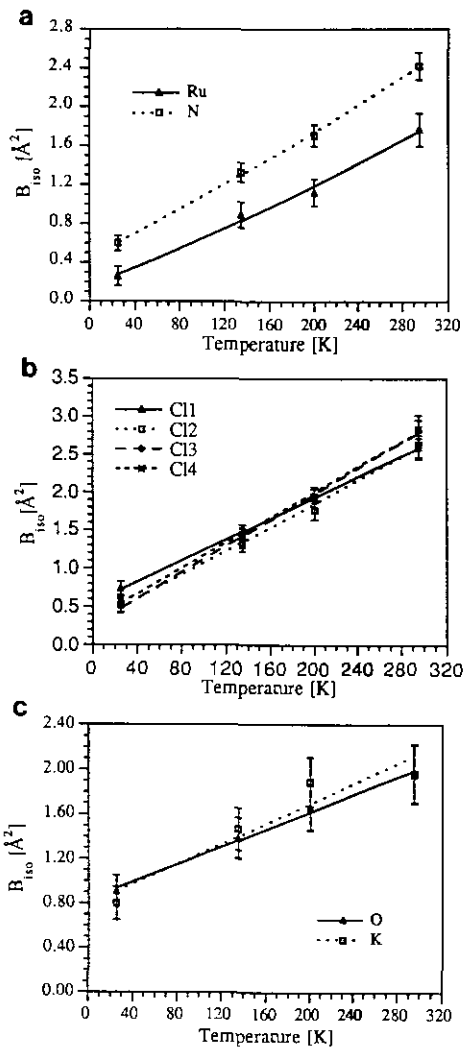

FIG. 3. Temperature dependencies of isotropic temperature factors (a) for Ru and N, (b) for the chlorine atoms, the equatorial as well as the axial Cl_2, and (c) for O and K of $K_2[RuCl_5NO]$.

TABLE IV

TEMPERATURE DEPENDENCES OF THE MAIN BOND LENGTHS [Å] AND BOND ANGLES [°] OF THE $[RuCl_5NO]^{2-}$ MOLECULE IN $K_2[RuCl_5NO]$

T [K]	295	200	135	25
Ru–N	1.759(12)	1.746(10)	1.741(9)	1.723(8)
N–O	1.100(13)	1.110(11)	1.115(10)	1.131(9)
$Ru–Cl_1$	2.413(11)	2.423(9)	2.414(8)	2.402(7)
$Ru–Cl_2$	2.356(12)	2.366(10)	2.374(9)	2.390(8)
$Ru–Cl_3$	2.381(11)	2.369(9)	2.370(8)	2.378(7)
$Ru–Cl_4$	2.356(4)	2.363(3)	2.365(3)	2.372(3)
N–Ru–O	175.3(10)	175.3(8)	175.5(7)	175.2(6)
$Cl_2–Ru–N$	176.8(6)	176.9(5)	176.6(5)	176.5(4)
$Cl_1–Ru–N$	94.2(5)	94.8(4)	94.9(4)	95.6(3)
$Cl_3–Ru–N$	89.8(4)	89.9(4)	89.9(3)	89.6(3)
$Cl_4–Ru–N$	91.9(2)	92.3(2)	92.6(2)	92.4(2)
$Cl_2–Ru–Cl_1$	89.0(4)	88.4(3)	88.4(3)	87.9(2)

The bondlengths at 295 K measured by means of neutron diffraction agree with most of the X-ray data (*7, 8*). We determined the bond distances $Ru–Cl_1$ = 2.41(1) Å and Ru–N = 1.76(1) Å, close to the values of 2.377(2) Å and 1.747(6) Å, respectively, found by Veal and Hodgson (*9*). The shortest distance from K is 3.27(1) Å to Cl_4 at 295 K.

For lower temperatures the bond angles differ more and more from the ideal C_{4v} symmetry. The maximum deviation found is 1.1(4)° for the $Cl_2–Ru–Cl_1$ angle at 25 K. A striking fact is that for $K_2[RuCl_5NO]$ and sodium nitroprusside the ligand–metal–(NO) bond angle is identical, 176.8(6)°, while for all other angles the $[RuCl_5NO]^{2-}$ molecule is closer to the C_{4v} symmetry. The observed equatorial bonds in $K_2[RuCl_5NO]$ differ and their temperature dependencies are not uniform.

Discussion

By means of neutron diffraction experiments on a powder sample of $K_2[RuCl_5NO]$ the temperature dependence of the crystal structure was established in the temperature range from 25 to 295 K. The symmetry corresponds to the orthorhombic space group *Pnma*. Neither a structural nor a magnetic phase transition was detected within the investigated temperature range. A similar behavior of isotropic temperature factors and bondlengths of the $[RuCl_5NO]^{2-}$ molecule was found. The determined isotropic temperature factors indicate an additional libration around the distinguished $Cl_2–Ru–N–O$ axis. All bondlengths change smoothly; some decrease ($Ru–Cl_2$), while others increase (Ru–N) from 25 to 295 K. No saturation of the unit cell volume at low temperatures was found. It is planned to extend the measurements to lower temperatures.

Acknowledgments

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