

in concentration of complexes. Since polymerization and depolymerization occur very slowly in Co(III) complexes, the ^{59}Co line widths will not be affected even if a small amount of polymeric species is produced by *olation*. In the present experiments any signals which correspond to polymeric species were not detected, suggesting that in the present Co(III) system *olation* does not occur even in highly concentrated region.

It should be noted that the ^{59}Co line width for $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ is one order of magnitude smaller than that for $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$. Hartmann and Sillescu⁹ reported a nuclear quadrupole coupling constant of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ ($e^2qQ/h = 54.8$ MHz at 298 K), while no data have been obtained for $[\text{Co}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$. According to the method of Hartmann and Sillescu,⁹ the nuclear quadrupole coupling constant for $[\text{Co}(\text{NH}_3)_5\text{OH}]\text{X}_2$ is estimated at 16 MHz from the ^{59}Co line width in solution. This large difference in e^2qQ/h seems to be closely related to a difference in nature between the Co-OH and Co-OH₂ bonds. Hartmann and Sillescu⁹ reported a ^{59}Co line width of 1.15 G for $[\text{Co}(\text{NH}_3)_5\text{OH}](\text{NO}_3)_2$ in aqueous solution. In the case of $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$, the change in the line width with the counter anions (Cl^- , ClO_4^- , and NO_3^-) and the concentration of the complex (from 0.1 to 0.4 M) is small (≤ 0.5 G for the aquo complex and ≤ 0.05 G for the hydroxo complex).¹⁰ In view of these results this large line width, 1.15 G, seems to suggest that in aqueous solution $[\text{Co}(\text{NH}_3)_5\text{OH}](\text{NO}_3)_2$ is protonated to yield a considerable amount of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ ion.

The ^{59}Co chemical shifts can be used to estimate the rate of proton exchange between the aquo and hydroxo complexes. A sharp single line is observed for a solution containing $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ ions. With the use of the chemical shift difference, 1080 Hz, between these ions, the lower limit of the rate constant for the acid dissociation, k_a , and that for the reverse reaction, k_{-a} , are estimated at 10^8 sec⁻¹ and 10^9 M⁻¹ sec⁻¹, respectively. These results are to be compared with $k_a = 1.1 \times 10^5$ sec⁻¹ and $k_{-a} = 9.6 \times 10^8$ M⁻¹ sec⁻¹ which have been obtained for the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion by means of the spin-echo technique.¹¹

Acknowledgment.—The authors wish to thank Dr. Y. Arata and Dr. T. Yamamoto for helpful discussions. Thanks are also due to Mr. K. Nakamura, National Research Institute for Metals, for the use of a Varian nmr spectrometer.

(9) H. Hartmann and H. Sillescu, *Theor. Chim. Acta*, **2**, 371 (1964).

(10) F. Yajima and S. Fujiwara, unpublished data.

(11) D.-W. Fong and E. Grunwald, *J. Amer. Chem. Soc.*, **91**, 2413 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MISSOURI, COLUMBIA, MISSOURI 65201

The Structure of Crystalline Potassium Dioxotetracyanorhenium(V), $\text{K}_3\text{ReO}_2(\text{CN})_4$

BY R. KENT MURMANN AND ELMER O. SCHLEMPER*

Received February 26, 1971

Compared to the large number of tetraoxo ions (MO_4^{n-}) which are known, the number of dioxo ions

which have been characterized is small. It can also be stated that few studies on the latter type ion have been made, and thus our chemical and physical knowledge is slim. A chemical study on the ^{18}O -exchange kinetics and some reactions of $\text{K}_3\text{ReO}_2(\text{CN})_4$ has just been concluded¹ which brought to light the facile conversion of $\text{ReO}_2(\text{CN})_4^{3-}$ into a dimer thought to be $\text{ORE}(\text{CN})_4\text{ORE}(\text{CN})_4\text{O}^{4-}$. A single-crystal X-ray structure determination was begun on a salt of the latter ion. This determination is now complete and will be communicated in the near future. For comparison, the molecular parameters were needed for $\text{ReO}_2(\text{CN})_4^{3-}$. Such a structure determination was reported in 1961,² and our original intent was to improve upon the precision of the molecular parameters using more modern methods of data collection and computation. The results of this study revealed differences in the unit cell and much improved the precision in bond distances and angles in the ion. The improvement in the precision allows direct comparison with the dimeric complex ion whose structure will be presented later.

Experimental Section

Crystal Preparation.— $\text{K}_3\text{ReO}_2(\text{CN})_4$ was prepared from $\text{Re}(\text{en})_2\text{O}_2^{2+}$ by the method previously described.³ After purification¹ a final slow crystallization from water gave well-formed anhydrous crystals.

X-Ray Data.—Potassium dioxotetracyanorhenium(V), $\text{K}_3\text{ReO}_2(\text{CN})_4$, crystallizes in the triclinic system with cell dimensions, as determined by careful centering of 23 reflections on a Picker diffractometer using Mo K α radiation and a narrow vertical slit at the counter, of $a = 7.470 \pm 0.002$ Å, $b = 7.597 \pm 0.002$ Å, $c = 6.329 \pm 0.002$ Å, $\alpha = 105.37 \pm 0.02^\circ$, $\beta = 110.20 \pm 0.02^\circ$, $\gamma = 114.63 \pm 0.02^\circ$, and $V = 268.9 \pm 0.1$ Å³. These are the reduced cell dimensions from a Delauney reduction⁴ of an unconventional cell. The density calculated on the basis of one formula per unit cell, 2.715 g/cm³, is in good agreement with the reported density⁵ of 2.704 g/cm³.

These cell dimensions are not the same as those reported by earlier workers,² possibly due to a different choice of axes. The dimensions reported were $a = 7.35 \pm 0.02$ Å, $b = 7.73 \pm 0.02$ Å, $c = 6.32 \pm 0.02$ Å, $\alpha = 108.3 \pm 0.2^\circ$, $\beta = 107.5 \pm 0.2^\circ$, $\gamma = 114.3 \pm 0.2^\circ$, and $V = 269.5$ Å³; a and b as well as α and β have been interchanged from the original paper for comparison. The cell volumes are nearly identical, but the a and b dimensions are significantly different. We have applied the Delauney method to both cells giving the reduced cells above. Yet the observed differences in angles and distances give different axis systems, as suggested by K1 being at $0, 1/2, 1/2$ in our cell and $0, 1/2, 0$ in the previous determination.

Intensities of some 4700 reflections, a complete sphere out to $2\theta = 65^\circ$, were measured using Mo K α radiation with a niobium β filter on a Picker four-angle programmer system. The intensity data were collected at a 2° takeoff angle using a θ - 2θ scan at scan rate of 1.0°/min. The scan length ranged from 1.00 to 1.35° in 2θ to account for the increasing width due to α_1 - α_2 splitting. Stationary counter backgrounds were taken for 20 sec on each side of the scan. Automatic attenuation was employed to prevent exceeding about 8000 cps during the scan. One-mil brass foils were used as attenuators to give attenuator factors of about 3. The pulse height selector was set for about a 95% window, centered on the Mo K α peaks. The receiving aper-

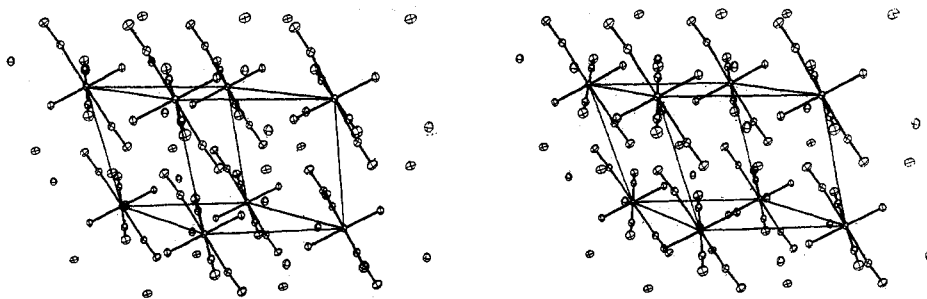
(1) D. L. Toppen, Ph.D. Thesis, University of Missouri, 1970; *Inorg. Nucl. Lett.*, **6**, 139 (1970).

(2) K. Lukaszewicz and T. Glowiak, *Bull. Acad. Polon. Sci.*, **9**, 613 (1961).

(3) J. H. Beard, C. Calhoun, J. Casey, and R. K. Murmann, *J. Amer. Chem. Soc.*, **90**, 3389 (1968).

(4) This and all other calculations were done on the IBM 360/65 computer of the University of Missouri Computer Research Center using the following programs: J. Ibers' TRACERA Delauney reduction program; W. Hamilton's HORSE general absorption correction program; W. Hamilton and J. Ibers' NUFK Picker input program; A. Zalkin's FORDAP Fourier program; W. Busing, H. Levy, R. Doedens, and J. Ibers' NUCLS least-squares program; W. Busing and H. Levy's ORFFE function and error program; C. Johnson's ORTEP ellipsoid plot program; and local data processing programs.

(5) W. Klemm and G. Frischmuth, *Z. Anorg. Allg. Chem.*, **230**, 215 (1937).

Figure 1.—Stereoview of eight formula weights of $K_3ReO_2(CN)_4$, which includes the complete unit cell.TABLE I
Positional and Thermal Parameters^a for $K_3ReO_2(CN)_4$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0	0	0	980 (5)	1118 (5)	1423 (7)	610 (4)	692 (4)	681 (4)
K1	0	1/2	1/2	145 (2)	145 (2)	294 (4)	76 (2)	80 (3)	111 (2)
K2	-3618 (1)	-1635 (1)	2942 (2)	171 (2)	196 (2)	227 (2)	107 (2)	112 (2)	110 (2)
O	275 (4)	1370 (4)	2968 (5)	155 (6)	154 (5)	167 (7)	86 (5)	92 (6)	75 (5)
C1	1213 (6)	2946 (6)	-339 (7)	150 (8)	148 (7)	201 (10)	85 (6)	98 (7)	92 (7)
C2	3490 (6)	1000 (6)	1994 (6)	127 (7)	157 (7)	198 (10)	84 (6)	95 (7)	98 (7)
N1	1983 (7)	4480 (6)	-611 (8)	230 (10)	183 (8)	331 (13)	109 (8)	148 (10)	162 (9)
N2	5398 (6)	1600 (7)	3117 (8)	140 (8)	226 (9)	324 (13)	102 (7)	106 (9)	124 (9)

Root-Mean-Square Components of Thermal Displacement along the Principal Axes, Å

Atom	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
Re	1224 (7)	1342 (18)	1463 (4)	C1	1536 (54)	1604 (72)	1692 (30)
K1	1568 (41)	1575 (42)	2186 (14)	C2	1372 (42)	1553 (40)	1745 (37)
K2	1579 (13)	1745 (17)	1917 (8)	N1	1560 (43)	2016 (40)	2212 (45)
O	1454 (33)	1625 (44)	1723 (33)	N2	1485 (45)	2092 (46)	2185 (47)

^a The standard deviations from the least-squares refinement are included in parentheses. All parameters are $\times 10^4$ except the β 's for Re which are $\times 10^6$. The form of the thermal ellipsoids is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

ture at the scintillation counter was 3 mm \times 3 mm and was positioned 27 cm from the crystal. Three standard reflections were measured approximately every 50 reflections. A systematic increase in intensity, totaling 9%, was observed for about the first 2000 reflections, and those reflections were corrected using a linear relationship.

The data were corrected for background and Lorentz-polarization with a local program which uses the same approach as that of Corfield, Doedens, and Ibers.⁶ The crystal was bounded by 10 faces and was about 0.1 \times 0.2 \times 0.2 mm in dimensions. Absorption corrections were made ($\mu = 130.3 \text{ cm}^{-1}$) with the correction ranging from 0.26 to 0.38. Equivalent and duplicate reflections were then averaged to give 1902 independent reflections.

Determination of Structure.—All calculations⁴ were done on the IBM 360/65 computer of the University of Missouri Computer Research Center. Atomic scattering factors for neutral atoms were used. Those^{7a} for rhenium were taken from Cromer and Waber and include a correction for $\Delta f'$ and $\Delta f''$ in F_o ,^{7b} while all other scattering factors were from ref 7d.

The structure was solved completely from a Patterson synthesis since the rhenium atom is located at the origin of the unit cell. At this point the space group $P\bar{1}$ appeared to be the correct choice; this was subsequently confirmed by the refinement. Half of the anion is related to the other half by the center of symmetry at the rhenium. One of the potassium atoms is also located on a symmetry center.

Isotropic full-matrix least-squares refinement of this model converged with $R = \sum |F_o| - kF_c|/kF_o^2 = 0.089$ and $r = [\sum w(F_o^2 - kF_c^2)^2/\sum wF_o^4]^{1/2} = 0.126$. All refinements included a refinement of an isotropic extinction parameter.⁸ An all anisotropic refinement converged with $R = 0.051$ and $r = 0.058$. The conventional agreement factor ($= \sum |F_o| - |F_c|/\sum F_o$) was 0.023. The standard deviation of an observation of unit weight

was 1.38 with $\sigma(F_o^2) = [\sigma^2(\text{counting statistics}) + (0.040F_o^2)^2]^{1/2}$ and $w = 1/\sigma^2$.

A Fourier synthesis using the observed structure factor magnitudes showed the weakest carbon atom to have a peak density of $5.7 \text{ e}^-/\text{\AA}^3$. A final difference Fourier revealed no residual electron density greater than $1.2 \text{ e}^-/\text{\AA}^3$ except in the near vicinity of the rhenium atom, where the density reached a maximum of $3.1 \text{ e}^-/\text{\AA}^3$.

The observed and calculated structure factors appear in the microfilm edition of this journal.⁹

The final positional and thermal parameters are in Table I.

Results

Nature of the Structure.—The unit cell contains discrete ions, K^+ and $ReO_2(CN)_4^{3-}$. The rhenium atom is on a center of symmetry requiring a linear O-Re-O grouping. The coordination geometry about the rhenium is nearly octahedral with the largest deviation from 90° X-Re-X angles being 2° . The stereoscopic crystal structure is illustrated in Figure 1 where eight formula units are shown.

The potassium ions make close contacts with N and O atoms of the cation as given in Table II. The coordination about K1 is distorted octahedral with two nearest neighbor oxygens and four nitrogens with bond angles ranging from 76.4 to 103.6° . The coordination about K2 is much less regular with four nearest neighbors at about 2.8 \AA and two at about 3.2 \AA . Each nitrogen and oxygen of the anion are in close contact with three potassium ions.

Cyanide ion bonding to rhenium through the carbon

(9) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

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

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

(b) D. T. Cromer, *ibid.*, **18**, 17 (1965); (c) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964); (d) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(8) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

TABLE II
 INTERATOMIC DISTANCES AND ANGLES

Distance	Value, Å	Angle	Value, deg
Re-O	1.781 (3)-1.87 ^a	Cl-Re-C2	87.9 (1)
Re-Cl	2.139 (3)-1.91 ^a	Cl-Re-O	91.5 (1)
Re-C2	2.130 (3)-1.91 ^a	C2-Re-O	90.1 (1)
Cl-N1	1.156 (5)-1.15 ^a	Re-Cl-N1	173.4 (3)
C2-N2	1.154 (5)	Re-C2-N2	178.1 (5)
K1-N1	2.880 (4)	N2-K1-O	82.7 (3)
K1-N2	2.837 (4)	N1-K1-N2	85.2 (3)
K1-O	2.842 (3)	N1-K1-O	76.4 (3)
K2-O	2.843 (3)	O-K2-N1	122.9 (3)
K2-N1	2.803 (4)	O-K2-O	83.1 (3)
K2-N2	2.830 (4)	O-K2-N2	126.3 (3)
K2-N2	3.206 (4)	O-K2-N1	72.4 (3)
K2-O	2.796 (3)	O-K2-N2	76.4 (3)
		N1-K2-N2	101.0 (3)
		O-K2-N1	138.5 (3)
		N1-K2-N1	83.2 (3)
		N1-K2-N2	84.7 (3)
		N2-K2-O	82.8 (3)
		N2-K2-N1	148.7 (3)
		N2-K2-N2	78.9 (3)
		O-K2-N1	74.4 (3)
		O-K2-N2	135.9 (3)
		N1-K2-N2	132.4 (3)

^a Values reported in ref 2.

atom was confirmed by refinement of the isocyanide configuration. The resulting agreement factors, $R = 0.057$ and $r = 0.069$, were significantly poorer than with the cyanide arrangement and the thermal parameters were less reasonable in that the atoms attached to the rhenium displayed greater thermal motion than the external atoms.

The thermal ellipsoids are illustrated in Figures 1 and 2. The rhenium atom is nearly isotropic. Its maxi-

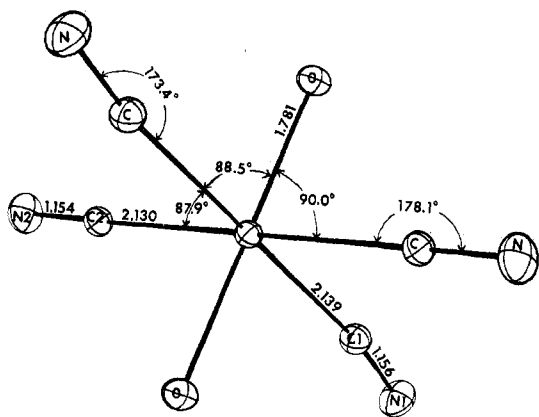


Figure 2.—Bond angles and distances in the ion $\text{ReO}_2(\text{CN})_4^{3-}$.

mum vibration nearly bisects the Cl-Re-O angle. For the carbon, nitrogen, and oxygen atoms the maximum vibration is essentially perpendicular to the bonds with the minimum directed along the bonds.

Bond Distances and Angles.—The average potassium to oxygen distance (2.83 Å) and potassium to nitrogen distance (2.96 Å) are typical¹⁰ ionic contacts. The C-N distances (1.155 (5) Å) are also quite typical. The deviation from 180° for the Re-C-N angles is due either to packing considerations or to interactions with the potassium ions. The 4.7° difference in these angles may come about through the nonequivalent interaction with potassium ions (Figure 1). Similar deviations from 180° Re-C-N angles have been ob-

(10) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 258.

served¹¹ in $[\text{Pt}(\text{NH}_3)_4]_2[\text{Re}_2\text{O}_3(\text{CN})_8]$. The Re-O distance (1.781 (3) Å) here reported is probably the best value known for a rhenium-oxygen "double bond" and is significantly longer than the multiple Re-O bond observed¹² in $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ReBr}_4\text{O}(\text{OH}_2)]$ of 1.71 (4) Å.

Conclusion

The crystal structure of $\text{K}_3\text{ReO}_2(\text{CN})_4$ has been re-determined and shows significant differences from the earlier study. The basic structure of the negative ion was confirmed and the accuracy and precision of the bond angles and distances were significantly improved. In a subsequent communication comparison of these anion parameters with those of $\text{ORe}(\text{CN})_4\text{ORe}(\text{CN})_4\text{O}^{4-}$ will be made.¹¹

(11) R. Shandles, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, in press.

(12) F. A. Cotton and S. J. Lippard, *ibid.*, **4**, 1621 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98105

Reactions of Peroxydisulfuryl Difluoride To Give Oxyfluorosulfates of Metals in High Oxidation State

BY RAJENDAR DEV AND GEORGE H. CADY*

Received February 1, 1971

There are a number of routes by which inorganic fluorosulfates have been prepared.¹⁻⁶

Peroxydisulfuryl difluoride has been shown to be an efficient sulfonating and oxidizing agent.⁶ Until recently a very few fluorosulfates of transition metals were known, particularly in their higher oxidation states. This paper reports the syntheses of oxyfluorosulfates of several transition metals in their higher oxidation states.

Experimental Section

Materials.—Peroxydisulfuryl difluoride was prepared by the reaction of fluorine with sulfur trioxide⁷ and purified by prolonged pumping of the crude product held at -78° . Its analysis and vapor density measurements indicated that the product was substantially pure.

The carbonates of manganese, cobalt, nickel, silver, and thallium of Baker Analyzed reagent grade were dried in an oven at 110° for 2 hr before use. Silver oxide was obtained by heating silver carbonate.

Preparation of Oxyfluorosulfates.—In a typical preparation, a known weight of the carbonate or oxide of the metal was treated in a closed glass vessel with an excess of peroxydisulfuryl difluoride. The latter was condensed into the reactor at -183° and the vessel was then allowed to warm to room temperature and stand for 3-12 hr. After the reaction appeared to be complete, the vessel was held at -40° while the volatile products were pumped away. These were later separated by fractional codistillation.⁸ The nonvolatile products were dried under vacuum to constant weight. The weights of oxyfluorosulfates obtained from the respective metal carbonate or oxide are given in Table I.

(1) O. Ruff, *Ber.*, **47**, 656 (1914).

(2) W. Traube, *ibid.*, **46**, 2513 (1913).

(3) E. Hayek, A. Czaloun, and B. Krismer, *Monatsh. Chem.*, **87**, 741 (1956).

(4) E. L. Muetterties and D. D. Coffmann, *J. Amer. Chem. Soc.*, **80**, 5914 (1958).

(5) A. A. Woolf, *J. Chem. Soc.*, 1053 (1950).

(6) J. M. Shreeve and G. H. Cady, *J. Amer. Chem. Soc.*, **83**, 4521 (1961).

(7) F. B. Dudley and G. H. Cady, *ibid.*, **79**, 513 (1957).