CHEMISTRY

E. I. KRYLOV, V. A. SAMARINA, and A. K. SHTOL' TS

1960

SovietRxiv

Abstract

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ON THE ISOMERISM OF COPPER SALTS OF NIOBIUM AND TANTALUM ACIDS

(Presented by Academician V. I. Spitsyn on 15 IX 1959)

Copper salts of niobic acids can be obtained by two different routes:

$$Cu_2O + Nb_2O_5 \xrightarrow{1000^\circ} 2Cu^+Nb^{5+}O_3, \qquad (1a)$$

$$CuO + NbO_2 \xrightarrow{700^\circ} Cu^{2+}Nb^{4+}O_3. \qquad (2a)$$

Analogous reactions are also possible for obtaining the corresponding tantalum preparations:

$$Cu_2O + Ta_2O_5 \xrightarrow{1000^\circ} 2Cu^+Ta^{5+}O_3, \qquad (1\ )$$

$$CuO + TaO_2 \xrightarrow{700^\circ} Cu^{2+}Ta^{4+}O_3. \qquad (2\ )$$

There is reason to believe that the products of these reactions will not be identical. For example, as the corresponding calculations show, the additively calculated densities of these compounds differ from one another, namely:

$$d_{(1a)} = \frac{\text{Mol. wt. } CuNbO_3}{\frac{1}{2}\left[(MV)_{Cu_2O} + (MV)_{Nb_2O_5}\right]} \simeq 5.0,$$

$$d_{(2a)} = \frac{\text{Mol. wt. } CuNbO_3}{(MV)_{CuO} + (MV)_{NbO_2}} \simeq 5.5.$$

A substantial difference may also be expected in the manifestation of magnetic properties. Compound (1a) should be diamagnetic, since neither the Cu^+ ion (d^{10}) nor the Nb^{5+} ion (d^0) has unpaired electrons. In compound (2a), both ions, Cu^{2+} (d^9) and Nb^{4+} (d^1), contain one unpaired electron each that does not participate in the formation of the chemical bond. Therefore preparation (2a) should be paramagnetic.

It seemed of interest to obtain the two above-mentioned series of copper compounds with niobium and tantalum acids and to establish the valence states of the elements entering into their composition. The present communication presents the results of investigations concerning the synthesis and identification of copper salts of niobic and tantalic acids by methods of magnetochemistry and X-ray phase analysis.

The niobium pentoxide used in this investigation was purified and analyzed by methods described earlier (1). The method for purifying tantalum pentoxide is given in work (2). The preparation of niobium and tantalum dioxides and the methods of their analysis were reported in article (3). Samples of cuproniobate (1a), or, respectively, cuprotantalate (1), were obtained by sintering equimolecular amounts of Cu_2O and Nb_2O_5 (or Cu_2O and Ta_2O_5) in vacuum.

(10^{-3} mm Hg) at 1000° for 8 h. The interaction between copper oxide and niobium (or tantalum) dioxide was also carried out in vacuum (10^{-3} mm Hg), but at a temperature of 700°. The substances obtained were analyzed for copper and niobium (tantalum) content. A sample of the substance of about 0.2 g was fused with a tenfold amount of potassium pyrosulfate. After cooling, the melt was leached with a 4% solution of tartaric acid. By electrolysis of this solution, copper was first deposited on the cathode, and then, after dissolving the washed cathodic deposit in $2N\ H_2SO_4$, it was determined iodometrically. Niobium, or correspondingly tantalum, was determined in the electrolyte after separation of the copper by the procedure described in [4]. The results of the analysis and of determining the density of the compounds obtained by the pycnometric method in toluene are presented in Table 1.

Table 1

Composition and density of copper salts of niobic and tantalic acids

No.	Compounds	Cu, found, %	Cu, calculated, %	Nb (Ta), found, %	Nb (Ta), calculated, %	Density, g/cm^3 at 18°	Color
1a	$Cu^{+}Nb^{5+}O_3$	30.04	31.07	46.8	45.44	5.1	Orange-brown
2a	$Cu^{2+}Nb^{4+}O_3$	32.17	31.07	44.3	45.44	5.3	Tobacco-colored
1b	$Cu^{+}Ta^{5+}O_3$	21.35	21.71	62.2	61.88	7.7	Light brown
2b	$Cu^{2+}Ta^{4+}O_3$	21.29	21.71	61.9	61.88	7.8	Dark brown

The analytical data show that, upon sintering niobium (tantalum) and copper oxides of different valences, products of identical composition are indeed

X-ray powder patterns

Figure 1: X-ray powder patterns

formed. The densities of the preparations obtained are close to those calculated from molecular volumes. These compounds are stable and do not dissolve in concentrated solutions of mineral acids. For identification of the synthesized and starting substances, X-ray powder patterns were taken in X-ray cameras with a cassette diameter of 57.3 mm.

Fig. 1. X-ray patterns of oxygen compounds of copper and niobium:
I –CuO; *II* –NbO_2; *III* –$Cu^{2+}Nb^{4+}O_3$; *IV* –$Cu^{+}Nb^{5+}O_3$;
V –Cu_2O; *VI* –Nb_2O_5

The exposures were made mainly with Co $K_{\alpha,\beta}$ radiation. In all, 18 X-ray patterns were obtained, some of which were taken with copper radiation. The most characteristic results of the calculation of the X-ray patterns are given in Fig. 1. From a comparison of X-ray patterns *I*, *II*, and *III* it is evident that *III* is the X-ray pattern of a new chemical compound (2a). The lines of CuO (*I*) and NbO_2

(II), although they are present on X-ray pattern III, but differ in their weak intensity. On X-ray pattern III there are very weak lines of cuprous oxide (V), probably formed upon heating copper oxide, but they disappear after washing the sample with acetic acid. From comparison of the X-ray patterns of $Cu^{+}Nb^{5+}O_3$ (IV) with Cu_2O (V) and Nb_2O_5 (VI), it is evident that the lines corresponding to the starting substances are absent from X-ray pattern IV; thus, the individuality of compound (1a) also gives no cause for doubt.

Table 2

Substance	$\chi_g \cdot 10^6$	$\chi_g \cdot 10^6$	$\chi_g \cdot 10^6$	$\chi_{\text{mol}} \cdot 10^6$	$\chi_{\text{mol}} \cdot 10^6$	$\chi_{\text{mol}} \cdot 10^6$
	90°K	206°K	290°K	90°K	206°K	290°K
$Cu^{2+}Nb^{4+}O_3$	7.5	2.98	1.93	1630	710	490
$Cu^{2+}Ta^{4+}O_3$	1.0	0.3	0.28	1900	728	514

The magnetic susceptibility of all the substances obtained was measured by the Gouy method (^{5}) at 90, 206, and 290°K and at a magnetic-field strength H = 1900–2100 oersted. It was found that the compounds obtained from cuprous oxide and niobium pentoxide, or respectively from tantalum pentoxide, are diamagnetic. On this basis they may be assigned the formulas $Cu^{+}Nb^{5+}O_3$ and $Cu^{+}Ta^{5+}O_3$, since in these molecules there are no ions with unpaired electrons. The compounds obtained by interaction of copper oxide and niobium dioxide, or respectively tantalum dioxide, are paramagnetic. The experimental values of the magnetic susceptibility, recalculated per mole of substance with a correction for diamagnetism, are presented in Table 2. The experimental dependence of the magnetic susceptibility of these compounds on temperature follows the Curie law

$$\chi_{\text{mol}} = C_{\text{mol}}/T. \tag{1}$$

Having determined the Curie constant from equations (1), using the data of Table 2, one can calculate the average effective moments per one paramagnetic atom in the compounds studied:

$$\mu_{\text{eff}} = 2.84\sqrt{\frac{C_{\text{mol}}}{2}}.$$

Table 3

Values of the Curie constants and average effective moments of Cu^{2+}, Nb^{4+}, and Ta^{4+} ions in molecules

Compound	Curie constant	Effective moment	Effective moment
		per atom	per molecule
$Cu^{2+}Nb^{4+}O_3$	0.15	0.78	1.10
$Cu^{2+}Ta^{4+}O_3$	0.17	0.83	1.17

The calculated data are given in Table 3. The values of the average effective moments indicate the divalency of copper and the tetravalency of niobium and tantalum in these compounds. On the basis of the magnetic measurements and the chemical-analysis data, compounds (1a) and (1b) may be regarded as metaniobate and metatantalate of monovalent copper, and compounds (2a) and (2b) as niobate and tantalate of divalent copper. For these compounds it is essential that they are in a relation of valence isomerism.

Ural Polytechnic Institute
named after S. M. Kirov

Received
14 IX 1959

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Note: Figure translations are in progress. See original paper for figures.