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Abstract

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THE STRUCTURE OF RHODIUM ACETATE COMPLEXES

(Presented by Academician I. I. Chernyaev on 6 IV 1962)

In paper ([1]) a series of new compounds of rhodium of lower valence with formate groups was described, distinguished by great stability. Their chemical analysis, valence as determined by Noddack ([2]), and diamagnetism initially led to the conclusion that the substances obtained are compounds of monovalent rhodium. In addition to the simplest compound—rhodium formate, to which the composition $HRh^{I}(HCOO)_2 \cdot {}^1/_2H_2O$ (I) was assigned—the authors mention salts $NH_4Rh^{I}(HCOO)_2$, $PyHRh^{I}(HCOO)_2$, and others (however, it was not possible to obtain alkali-metal salts analogous to the ammonium and pyridine salts). Somewhat later L. A. Nazarova and co-workers synthesized a large group of rhodium compounds of similar composition with acetate groups, and in particular a well-crystallizing substance having the approximate composition $HRh^{I}(CH_3COO)_2 \cdot nH_2O$ or $Rh^{II}(CH_3COO)_2 \cdot nH_2O$ (II). Compounds I and II are close in chemical properties and form dark-green crystals similar in external habit. Both substances were supplied to us for an X-ray structural investigation. The present communication gives preliminary data on the crystal structure of the second of them—rhodium acetate.

Crystals of Rh acetate belong to the monoclinic system; the space group is $C_{2h}^6 = C\,2/c$. The lattice parameters, established from oscillation X-ray photographs, are: $a = 13.05$; $b = 8.60$; $c = 13.76$ Å; $\angle\beta = 118^\circ$. There are 8 formula units of monomeric composition per unit cell.

From projections of the interatomic function $P(uv)$, $P(uw)$, and $P(vw)$ it was established that rhodium atoms, connected in pairs by centers of inversion, are located at a distance of about 2.45 Å. The substance, consequently, is built of dimeric complexes. A projection of the electron density onto the plane (010) in the first approximation (with signs of the structural amplitudes calculated from the positions of the rhodium atoms) is shown in Fig. 1. The projection revealed the arrangement of two of the four acetate groups belonging to the dimeric molecule. These groups lie approximately in the plane of projection and serve as bridges connecting the two rhodium atoms. Judging from the concentration of maxima along the long diagonal of the depicted region of the projection, the two other CH_3COO^- groups are located in a plane perpendicular to the plane of the drawing and play an analogous role. Thus it became obvious that the rhodium

Fig. 1

Figure 1: Fig. 1

atoms are bound into dimers by four bridging acetate groups in the same way as was found for divalent copper acetate ([3]) and divalent chromium acetate ([4]). Comparison of the projection obtained with the analogous projection of divalent copper (Fig. 2), borrowed from work ([3]), leaves no doubt as to the complete isostructurality of the crystals of these compounds and, consequently, to the identity of the structure of the complexes.

Calculation of the molecular weight from the volume of the unit cell and the density, the geometric analogy of the lattices of rhodium and copper acetate, and, chiefly, the presence of corresponding maxima in the projection of the electron density prove that the crystals under study contain one molecule of water each.

for each rhodium atom. This conclusion was confirmed by chemical analysis. The positions of the maxima corresponding to water molecules show that they complete the coordination of the rhodium atom to octahedral: each Rh atom is bonded to four oxygen atoms, to the second rhodium atom, and to a water molecule.

The stereochemical result obtained at this stage of the investigation makes it possible to draw several general conclusions.

Fig. 1

1. On the basis of the structure found, and also taking into account the failure to obtain salts of alkali metals of composition $M[Rh(RCOO)_2] \cdot nH_2O$, it seems most probable that the ammonium and pyridinium salts mentioned above are in fact products of substitution of water molecules by ammonia and, respectively, pyridine. L. A. Nazarova and I. I. Chernyaev had already arrived at the same conclusion somewhat earlier on the basis of the chemical properties of the synthesized acetate compounds. It may also be noted that in the copper compound $Cu(CH_3COO)_2 \cdot Py$ the pyridine molecules play the same role as the water molecules in $Cu(CH_3COO)_2 \cdot H_2O$ ([5,12]).

2. Monovalent rhodium has an even number of its own electrons (not participating in bonds). Therefore the diamagnetism of the acetate compound with the complex anion $[Rh_2(CH_3COO)_4(H_2O)_2]^{2-}$ can be explained either by the absence of electron exchange between the rhodium atoms (which is almost incredible), or by assuming that such exchange is effected by two pairs of electrons. But with D_{4h} symmetry and with ten ligands, one of these pairs must inevitably be on an antibonding orbital that destabilizes the bond. Indeed, on the molecular orbitals obtained by combination of all the $4d$, $5s$, and $5p$ atomic orbitals of both rhodium

Fig. 2

Figure 2: Fig. 2

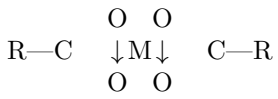
atoms and the corresponding orbitals of the ligands, 36 electrons must be accommodated, of which 16 do not participate in bonds with the oxygen atoms and water molecules. Of these, 12 are located on six nonbonding orbitals obtained from the d_{xy}, d_{xz}, and d_{yz} atomic orbitals of the Rh atoms, and four—on two orbitals obtained from the $d_{x^2-y^2}$ atomic orbitals of the Rh atoms; one of them is bonding, the other antibonding. Considering that the Rh—Rh distance, equal to 2.45 Å, is substantially smaller than in metallic rhodium, such an absence of effective contraction of the rhodium atoms seems unlikely.

These considerations lead to the idea that, in reality, the dimeric complex under consideration is neutral, i.e., the formal valence of rhodium in this compound is not one, but two. In this case both the diamagnetism and the shortening of the distance are naturally explained by the exchange of one pair of electrons entering the bonding molecular orbital*.

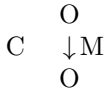
Fig. 2

The same conclusion—that there are no outer-sphere hydrogen atoms (divalency of rhodium)—was also reached by I. I. Chernyaev and co-workers after an additional, more detailed consideration of the chemical properties.

3. The principal cause of the instability of a monomeric planar structure of the type



with covalent *M*—*O* bonds, not only in the case of rhodium but also of other transition metals, is apparently the geometrical factor: in the four-membered ring



(with ordinary *C*—*O* and *O*—*M* bond lengths) the angles would be excessively distorted**. In particular, planar complexes of divalent platinum and palladium with such a structure can hardly be stable. On the contrary, the actinides, for which hexagonal-bipyramidal complexes with angles of 60° between bonds situated in the equatorial plane are characteristic, can form such four-membered rings with carbonate addends.

4. Apparently, compounds of transition metals with two covalently bound residues of carboxylic acids and with square or octahedral coordination of the metal can be divided into three groups: a) those with dimeric complexes, the stability of which is increased by an additional metal–metal bond; b) those with network or framework structures, in which the RCOO groups bind metal atoms into infinite polymers without formation of $M—M$ bonds; c) those with monomeric complexes, in which each RCOO group forms a bond with the metal atom through only one of the two oxygen atoms. The first group includes the acetates of copper ([3]), chromium ([4]),

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* This result can also be obtained by a simplified consideration of the electrons of only one of the two rhodium atoms (and of the ligands bonded to it) under the local symmetry of the C_{4v} field. The neutral complex gives a stable 18-electron system (9 electrons from the Rh atom, 6 from the oxygen atoms, 2 from the water molecules, and 1 from the second rhodium atom), whereas for the composition $H_2[Rh_2(CH_3COO)_4(H_2O)_2]$ 20 electrons would have to be placed in the molecular orbitals, and consequently two of them would be at an antibonding level.

** An exception is zinc acetate $Zn(CH_3COO)_2 2H_2O$, in which two water molecules and two acetate groups are adjacent to the metal atom, each through two oxygen atoms ([6]). Formally, the coordination of zinc is distorted octahedral. However, the $Zn—O$ distances, equal to 2.18 Å, are greater than would be expected for covalent bonds of this kind. Since tetrahedral arrangement of bonds is most characteristic for zinc, and the angle between $Zn—H_2O$ bonds is greater than a straight angle, it seems most plausible to interpret the complex as the result of ionic interaction of zinc with two acetate anions, considered as wholes and completing the coordination of the zinc atom to tetrahedral.

rhodium, and also, judging from anomalous magnetic properties ([7]), paramagnetic-resonance data ([8]), and dichroism ([9]), compounds of copper with residues of other, more complex carboxylic acids. To the second group belong the formates of copper ([10]), nickel, and cobalt: $Cu(HCOO)_2 \cdot 4H_2O$, $Ni(HCOO)_2 \cdot 2H_2O$, and $Co(HCOO)_2 \cdot 2H_2O$ (a partial structural study of the last two was carried out recently by A. S. Antsyshkina). To the third group belong the acetates of cobalt and nickel of composition $M(CH_3COO)_2 \cdot 4H_2O$ ([11]).

5. At present it is still difficult to judge what determines the difference in the structure of these compounds. Attention is drawn to the fact that dimeric complexes with a metal–metal bond have been found only for those three elements which, when described within the framework of crystal-field theory, are characterized by an odd number of electrons on the (upper) doublet d_γ level (high-spin chromium acetate–configuration $d_\varepsilon^3 d_\gamma^1$, low-spin rhodium acetate–configuration $d_\varepsilon^6 d_\gamma^1$, copper acetate–configuration $d_\varepsilon^6 d_\gamma^3$).

This circumstance suggests that the tendency to form such complexes is determined by the same tendency toward lowering the symmetry of the environment which leads to the distortion of octahedra around C(II) and C(II) atoms in ordinary (monomeric) complexes. If this is indeed so, then dimeric complexes should also be given by divalent iridium and by trivalent ruthenium and osmium.

As for the high-spin analogue of rhodium—divalent cobalt—here (as also in the case of nickel) the upper d_γ level is filled symmetrically and, accordingly, metal—metal bonds are not formed in acetate complexes. It is not entirely clear, however, what determines the rupture of the metal—metal bond in passing from the acetate to the formate compound of copper: the nature of the addends (i.e., fine nuances in the distribution of valence electrons in such groups) or the presence in the formate compounds studied (both copper and cobalt) of "extra" water molecules, which leads to such a rearrangement of atoms that the oxygen atoms of the HCOO groups become accessible for the formation of hydrogen bonds.

The difference found in several examples between the structures of acetate and formate compounds makes further structural study of rhodium formate highly relevant; despite the similarity of external appearance, color, and chemical properties, it is clearly different in structure from the acetate. If rhodium formate proves to be constructed similarly to the formates of other metals, then its diamagnetism can be explained only on the basis of the even number of electrons on the valence levels of each of the metal atoms, i.e., on the basis of the monovalency of rhodium.

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