*Contribution from the Institute of Chemistry University of Wrocław, Poland*

# The Structure of Oxotricobalt Acetate*

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*Received September 16, 1972*

*The product of the oxidation reaction of cobalt(II) acetate in anhydrous acetic acid solution has been investigated. The IR, UV and visible spectra as well as magnetic susceptibility measurements on cobalt complex are discussed.*

*According to those and polarographic and conductometric studies, the complex investigated has been reformulated as* $Co_3O(OAc)_6(HOAc)_3$.

## Introduction

While the dark green, relatively stable product of cobalt(II) acetate oxidation in anhydrous acetic acid has been known for many years, its composition and structure have not been definitely determined.

This compound, prepared by several methods, is considered to possess various structures, such as: monomeric $Co(OAc)_3$ or trimeric $Co_3(OAc)_9$ by Abegg et al;[1] a binuclear cationic structure $[(HOAc)_4Co(OH)_2Co(HOAc)_4]^{4+}$ suggested by Mori *et al*[2] or a dimetric structure $[(OAc)_2Co(OH)_2Co(OAc)_2]$ reported by Koubek and Edwards.[3] Recently Lande *et al*[4] have established that the composition of this complex in the solid phase corresponds to a formula $Co_2(OAc)_4$-$(OH)_2 . HOAc$.

In our earlier studies we have found that by applying different methods for synthesis, one may obtain the products of very similar spectroscopic (positions of the absorption bands) and magnetic (magnetic susceptibility) properties, although their compositions (quantitative analyses) may somewhat vary.[5] The present work is intended to elucidate the reasons of some divergencies in interpretation of the structure of $Co^{II}$ acetate oxidation product and to suggest a new approach to the structure of this compound.

## Experimental Section

*Procedures.* Oxotricobalt acetate was prepared by oxidation of $Co^{II}$ acetate (5 g) in anhydrous acetic acid (300 cc) with a mixture of ozone and oxygen (about 2% ozone by volume) passed through the solution at room temperature for 24 hours. A dark green solution obtained was passed over a specially prepared anion exchanger (Dowex Type 2×8) in order to purify it from unreacted $Co^{II}$, helpd up on the anionite as $[CoCl_4]^{2-}$.

The anionite was prepared as follows: first, it was washed with 2N HCl and then rinsed with water to neutral reaction and at last, with anhydrous acetic acid to remove water. The eluate was distilled in vacuo at temperatures up to 35°C yielding a thick oil from which dark green fine crystals were crystallized in a vacuum desiccator over KOH.

*Analytical determinations.* Found: Co, 24.08; C, 29.32; H, 4.09%. Calculated for $Co_3O(OAc)_6(HOAc)_3$: Co, 24.30; C, 29.73; H, 4.16%.

The molecular weight determined by the isopiestic method is $742.4 \pm 27$ (theoretical $M = 723.23$).

Conductometric titration with sodium hydroxide revealed three endpoints (3.27; 7.59; 9.45 gram-equivalents of NaOH per 1 mole of $Co_3O(OAc))_6(HOAc)_3$ corresponding to approximately 3, 6, 9 acetate ligands in one molecule.

*Measurements.* Electronic absorption spectra were recorded by means of Unicam SP-700 and SP-500 spectrophotometers and the IR spectra were obtained in a Perkin-Elmer Model 621 spectrophotometer. Magnetic susceptibility measurements in solid were made by the Gouy method. Thermogravimetric analyses were made over the temperature range from 25 to 1000°C in a derivatograph Type OD-102. Polarographic reduction in an acetate buffer (pH —4.2) was studied by means of a Type OH-102 polarograph.

## Results and Discussion

Elementary analysis of the $Co^{II}$ acetate oxidation product and the molecular weight determined permitted to establish its formula as $Co_3O(OAc)_3(HOAc)_6$.

An empirical formula of the cobalt complex allows the Co atom to appear at two different oxidation states (e.g. $1Co^{2+}$, $2Co^{3+}$ or $2Co^{2+}$, $1Co^{4+}$).

Quantitative determination of $Co^{III}$ in the complex has shown that the $Co^{III}/Co^{II}$ ratio is equal to 2. It was thus possible to assume a general formula $Co^{II}Co_2^{III}O(OAc)_6(HOAc)_3$ for the compound under investigation. The two different oxidation states of cobalt should be reflected in a specific course of the polarographic reduction.

*Polarographic reduction.* Studies on polarogra-

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(*) Paper presented at the XIVth ICCC, Toronto, Canada 1972, Proceedings p. 695-7.

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**Table I.**

| No | h (mm) | $[\bar{i}'_{lim}]\times10^7$ (A) | $[\bar{i}''_{lim}]\times10^7$ (A) | $\sqrt{\frac{h_{1,3}}{h_{2,4}}}$ | $\frac{[\bar{i}''_{lim}]_{1,3}}{[\bar{i}''_{lim}]_{2,4}}$ | $\frac{[\bar{i}'_{lim}]_{1,3}}{[\bar{i}'_{lim}]_{2,4}}$ |
|---|---|---|---|---|---|---|
| 1 | 60 | 18.5 | 44.2 | 1.10 | 1.10 | 1.11 |
| 2 | 49 | 16.8 | 39.7 | | | |
| 3 | 36 | 14.4 | 33.8 | 1.20 | 1.18 | 1.18 |
| 4 | 25 | 12.2 | 28,6 | | | |

**Table II.**

| Concentration $c\times10^4$, *M* | $[\bar{i}'_{lim}]\times10^7$ (A) | $[\bar{i}^s_{lim}]\times10^7$ (A) | $\frac{[\bar{i}^s_{lim}]}{[\bar{i}'_{lim}]}$ |
|---|---|---|---|
| 0.75 | 3.38 | 12.34 | 3.65 |
| 1.46 | 5.80 | 22.04 | 3.80 |
| 2.13 | 8.52 | 31.32 | 3.68 |
| 6.09 | 24.72 | 91.92 | 3.72 |
| 7.58 | 30.56 | 113.60 | 3.72 |

**Table III.**

| No. | Mode or drying (time, h) | Analysis. %Co | %C | Composition according to analysis | Magnetic data T °K | $\chi_g\times10^6$ | $\mu_{eff}$[a] [BM] | θ [°K] |
|---|---|---|---|---|---|---|---|---|
| 1. | KOH (24) | 23.77 | 28.64 | $Co_3O(OAc).(HOAc)_3$ | 294 | 7.63 | 2.11 | −2 |
| 2. | $Mg(ClO_4)_2$ (300) | 27.18 | 25.37 | $Co_3O(OAc)_6.(HOAc)_n$[b] | 291 | 10.54 | 2.48 | −43 |
| 3. | $P_2O_5$ (300) | 27.31 | 25.71 | $n = 1\div1.5$ | 294 | 11.89 | 2.49 | — |
| 4. | KOH (300) | 28.47 | 26.50 | | 293.7 | 12.26 | 2.63 | −56 |
| 5. | $CaCl_2$ (300) | 28.61 | 26.54 | | 291 | 13.16 | 2.50 | — |

[a] $\mu_{eff}$ were calculated from spin only formula and per Co - atom according to analysis. [b] for sample dried by heating from 25 125°C (5°C/min) partial decomposition of the complex was observed (analysis 38.66% Co and 19.71% C) as well as increasing of magnetic susceptibility and $\mu_{eff}$ ($\chi_g = 65.03\times10^{-6}$; $\mu_{eff} = 5.14$ BM at 289.7°K and θ = −43°K respectively).

phic reduction were performed with throughly deoxidized solutions of the cobalt complex (at $1.1\text{-}5.4\times10^{-5}$ *M* concentrations) in acetate buffer (pH = 4.2) at 25°C. Two reduction waves are observed, corresponding to a two-stage reduction of cobalt: (I) $Co^{3+}\rightarrow Co^{2+}$ and (II) $Co^{2+}\rightarrow Co^0$.

The shape of the second reduction wave (II) containing a low maximum whose intensity changes with the complex concentration is typical of $Co^{2+}$.[11]

The dependence of $\bar{i}'_{lim}$ (limiting current of the first wave) and $\bar{i}^s_{lim} = \bar{i}'_{lim}+\bar{i}''_{lim}$ (total current) on concentration is linear (satisfies the Ilkovic equation).

The limiting currents of the first and second reduction waves ($\bar{i}'_{lim}$ and $\bar{i}''_{lim}$) depend on the head of mercury (h) in a way which indicates their diffuse character (Table I).

The ratio of limiting currents $\bar{i}''_{lim}/\bar{i}'_{lim}$ or $\bar{i}^s_{lim}/\bar{i}'_{lim}$ depends on the ratio of $Co^{3+}/Co^{2+}$ in the complex. Assuming the ratio $Co^{3+}/Co^{2+} = 2$ as shown by the result of quantitative analysis the value of $\bar{i}^s_{lim}/\bar{i}'_{lim}$ should be expected to be equal to 4. Assuming $1Co^{3+}$ or $3Co^{3+}$ in the molecule, the ratio is $\bar{i}^s_{lim}/\bar{i}'_{lim}$ should be 7 and 3, respectively. As shown in Table II, the ratio $\bar{i}^s_{lim}/\bar{i}'_{lim}$ — for various concentrations is close to 4 which is another confirmation of the complex formula: $Co^{II}Co_2^{III}O(OAc)_6(HOAc)_3$.

*Magnetic properties.* Magnetic susceptibility is positive and varies differently with temperature for samples dried in different ways. A fresh complex (dried over KOH for 24 hours) has a susceptibility of $\chi_g = 7.63\times10^{-6}$ at 294°K while after continued drying in vacuum (for about 300 hours) it shows a slight increase in susceptibility (Table III).

Depending on the type of drying material used, the relationship $^1/\chi_g = f(T)$ is found to be linear or partialy nonlinear. According to the results presented in Table III and on Figure 1 there are no significant evidence for magnetic exchange between each pair of cobalts although the temperature variation of the experimental $\chi_g$ of samples dried intensively (No. 3, 5) can be due to some small exchange between cobaltous ions in adjacent trimeric units, when terminal acetic acid molecules are removed. The complex containing 3HOAc molecules coordinated in terminal positions has $\mu_{eff}$ = 2.11 B.M. (in solid and 2.16 B.M.

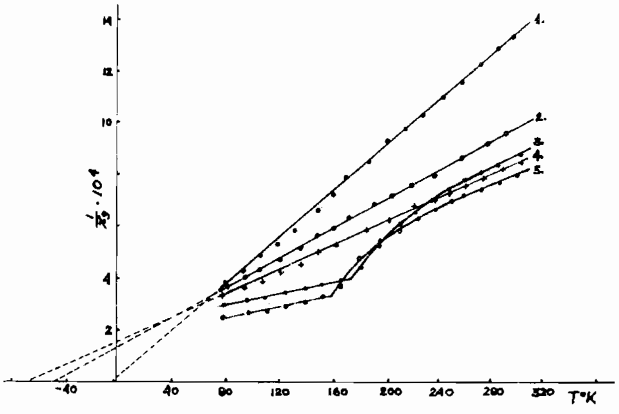

Figure 1. Magnetic susceptibility dependence on temperature for samples dried in different way: 1 - KOH, (24 h); 2 - Mg $(ClO_4)_2$, (300 h); 3 - $P_2O_5$, (300 h); 4 - KOH, (300) and 5 - $CaCl_2$, (300 h).

**Table IV.**

| Compound | ${}^3T_{1g}\leftarrow{}^1A_{1g}$; | ${}^3T_{2g}\leftarrow{}^1A_{1g}$; | ${}^1T_{1g}\leftarrow{}^1A_{1g}$; | ${}^1T_{2g}\leftarrow{}_1A_{1g}$ | C.T. | Ref. |
|---|---|---|---|---|---|---|
| $Co_3O(OAc)_6(HOAc)_3$ | | | | | | |
| in $H_2O$ | — | — | 16390 (324) | 29500 (2515) | | this |
| $C_2H_5OH$ | — | — | 16390 (358) | 29240 (2880) | 42700 | work |
| $CH_3COOH$ | — | — | 16130 (552) | 29240 (3505) | $(3\times10^4)$ | |
| $[Co(H_2O)_6]^{3+}$ | 8000 | 12500 | 16500 | 24700 | | [13] |
| $[Co\ ox_3]^{3-}$ | — | — | 16600 (125) | 23750 (155) | 41100 $(4.6\times10^4)$ | [14] |

**Table V.**

| Frequencies ($cm^{-1}$) KBr | Nujol | Assignments |
|---|---|---|
| 3010 m | | νCH |
| 2920 m | 2930 s | |
| 1700 m | 1705 s | νCOO |
| 1555 vs | 1565 vs | asym |
| 1415 vs | 1415 vs | νCOO |
| 1250 m | 1270 m | sym |
| 1344 s | 1345 s | $\delta CH_3$ |
| 1044 m | 1046 m | $\rho CH_3$ |
| 1025 m | 1030 m | rock |
| 940 vw | 950 w | νCC |
| 694 s | 656 s | δOCO, $\nu Co_3O$ |
| 625 s | 620 s | |
| 520 w | 580 m | ρCOO |
| 580 m | 523 | r |

(in anhydrous acetic acid solution, $\chi_g = 8.28\times10^{-6}$ at 300°K). Some increase of magnetic susceptibility is observed for samples containing less than 3HOAc per molecule (Table III).

Although the composition of $Co_3O(OAc)_6$ was never be obtained in this way, the complex of composition $Co_3O(OAc)_6(H_2O)_3$ was isolated by us as a product of reaction of anhydrous cobalt(II) acetate with acetaldehyde in the atmosphere of pure oxygen.[15] This complex is paramagnetic ($\mu_{eff} = 3.58$BM at 300 °K, $\theta = -10$°K) and unstable (particularly in water solution).

*Analysis*: found: Co(total), 29.15; $Co^{3+}$, 19.20%; calculated for $Co_3O(OAc)_6(H_2O)_3$: Co(total), 29.4; $Co^{3+}$, 19.46%.

It can be readily converted into $Co_3O(OAc)_6(HOAc)_3$ by recrystallization with anhydrous acetic acid.

*Thermogravimetric analysis.* Thermal decomposition of $Co_3O(OAc)_6(HOAc)_3$ was investigated by heating the sample up to 1000°C at a rate of 5°/min. The compound is stable up to 50°C and only over the temperature range from 50° to 125°C it is losing about 27.5% weight (slightly more than 3 HOAc). The loss of weight from 125 to 218°C is small (about 7.1%). Further loss of weight (about 31.9%) is observed from 225 to 365°C. Continuation of heating does not lead to any significant changes in the system (loss in weight about 2% at 920°C) and the residue (about 33.5%) is cobalt oxide (%Co found in the residue –78.9 calculated for $Co_3O_4$ –73.4%, for CoO –78.7%).

A scheme below illustrates the thermal decomposition process:

$$Co_3O(OAc)_6(HOAc)_3 \xrightarrow[-3HOAc]{50-125°} [Co_3O(OAc)_6] \xrightarrow[-(CH_3)_2CO]{125-218°}$$

$$\rightarrow [Co_3O(OAc)_4CO_3] \xrightarrow[-2(CH_3)_2CO,\ -3CO_2]{218-365°} Co_3O_4$$

The pattern of thermal decomposition shows that the liberation of 3HOAc is accompanied by continued decomposition of the complex and no pure $Co_3O(OAc)_6$ my be obtained by this method.

*Electronic absorption spectra.* The electronic absorption spectrum in anhydrous acetic acid is similar to that obtained by Lande *et al.*[4] and shows two absorption bands at 16130 $cm^{-1}$ (ε, 552), 29240 $cm^{-1}$ (ε, 3505). A similar shape has also the spectrum in aqueous solution and ethanol (Table IV). These bands may be assigned to spin-allowed transitions from the ground state ${}^1A_{1g}$ to ${}^1T_{1g}$ and ${}^1T_{2g}$, respectively, usually observed in low-spin hexacoordinated complexes of cobalt(III).

The position and intensities of these bands show some distortions of the octahedral symmetry, as compared to other spin-paired $Co^{III}$ complexes.

The two other bands corresponding to spin-forbidden transitions ${}^1A_{1g}\rightarrow{}^3T_{1g}$ and ${}^1A_{1g}\rightarrow{}^3T_{2g}$ found for some complexes at lower energies, are not observed in the compound under investigation while the band found at about 42700 $cm^{-1}$ (ε, ab. $3\times10^4$) may be described as a charge-transfer band (Table IV). Such type of spectra is observed for cobalt(III) complexes with oxygen ligands ($OH_2$, ox) (Table IV).

The contribution of $Co^{2+}$ to the spectrum could not be evaluated although one should expect two or three weak bands in the 8000-20000 $cm^{-1}$ region (ε, 1÷40 l, $cm^{-1}$ $mole^{-1}$) observed in hexacoordinated $Co^{II}$ complexes.[12] It seems that this results from a considerably higher $Co^{III}$ absorption in that region (ε, $10^2$-$10^3$). According to our measurements, the spectrum of ethanolic $Co(OAc)_2 . 4H_2O$ solution exhibits two bands at 8620 $cm^{-1}$ (ε, 2.4) and 19230 $cm^{-1}$ (ε, 11.6) which seems to support the above assumption.

*IR spectra.* The IR spectra in KBr disks and Nujol show a strong absorption corresponding to symmetric ($\nu^{COO}_{sym}$, 1415 $cm^{-1}$) and anti-symmetric ($\nu^{COO}_{asym}$, 1565 $cm^{-1}$) frequencies of the carboxyl group. In contrast to the data reported by Lande *et al.*,[4] we have found a medium band at about 1700 $cm^{-1}$ which corresponds to the anti-symmetric vibration of the carboxylic group in coordinated $CH_3COOH$ molecules (Table V). The intensity of this band decreases below 50% of the original value as the complex is being dried over potassium hydroxide.

## Final Remarks

$Co_3O(OAc)_6(HOAc)_3$ is an example of an oxotrimetal carboxylate containing an oxygen centered triangular framework. Similar complexes are well known for $Cr^{3+}$,[6] $Mn^{3+}$,[7] $Fe^{3+}$[8] and $Fe^{2+}$.[9] The structure of such a reformulated complex of cobalt is shown in Figure 2. According to this, each cobalt atom is coordinated with six oxygens, the central oxygen being coordinated by three cobalt atoms.

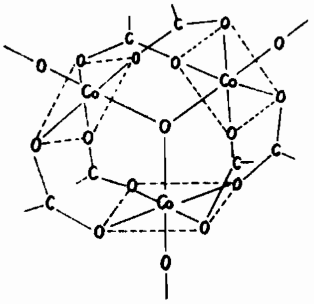

**Figure 2.** The structure of $Co_3O(OAc)_6(HOAc)_3$.

Considering the $M_3O$ nucleus according to Cotton *et al.*[10] as a unit of $D_{3h}$ symmetry and $C_3$ axis coinciding with the 'z' axis, one should assume that the triangular framework $Co_3O$ is formed by $3\sigma$ Co-O bonds.

Using a model suggested by Cotton *et al.* for $Ru_3O(OAc)_6(H_2O)_3^{+}$[10] and assuming that one of the linear combinations of 9 $t_{2g}$ orbitals will form a $\pi$-bonding with the $p_z$ orbital of oxygen,[15] a MO scheme may be suggested for the cobalt complex in order to elucidate its magnetic and spectroscopic properties (Figure 3). One should have in mind, however, a very qualitative nature of these considerations.

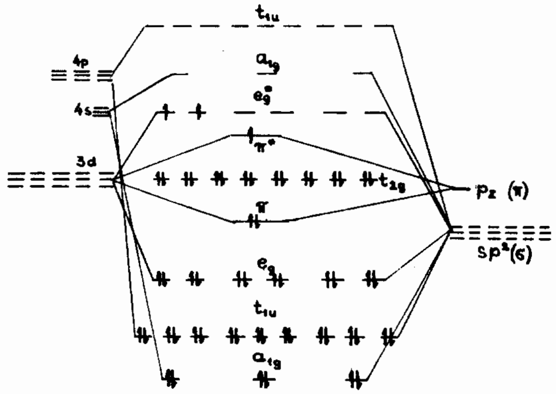

**Figure 3.** A qualitative molecular orbital diagram for $M_3O(OAc)_6X_3$ species. The electron distribution shown is that for $Co^{II}Co_2^{III}O(OAc)_6(HOAc)_3$.

Unsuccesful attempts to obtain a crystalline form of the complex may be explained as due to a strong intermolecular interaction, mainly because of the formation of hydrogen bonds between the acetic acid molecules in terminal positions. This is why the complex is so stable in anhydrous acetic acid.

*Acknowledgment.* The authors are indebted to Professor B. Jeżowska-Trzebiatowska for her interest in the work performed and to Dr. M. Ostern for help in the polarographic measurements.

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