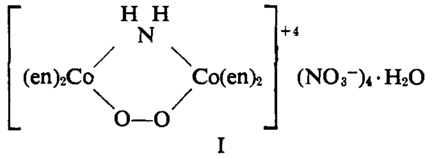
The Structures of the Cations of Werner's Green and Red μ-Amido-μ-peroxo-bis{bis(ethylenediamine)-cobalt(III)} Salts

Sir:

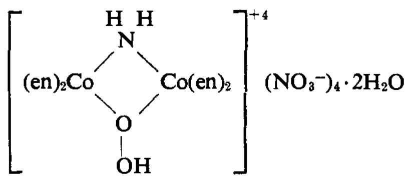
In 1910 Werner[1] described the preparations and chemical properties of a large number of bridged dicobalt compounds. Among them were two nitrate salts of doubly bridged cations, one red and the other green, which Werner presumed to be isomeric; the green compound he formulated as $[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_4$ and the red one as $[(en)_2Co(NH\cdot HNO_3)(O_2)Co(en)_2](NO_3)_3\cdot 2H_2O$. Isomerism was later ruled out when Malatesta[2] found the green compound to be paramagnetic, and Thompson and Wilmarth[3] found the red compound to be diamagnetic. Recently Mori and Weil,[4,5] on the basis of kinetic and spectroscopic measurements, inferred that the arrangement of the O_2 bridge is different in the two compounds and deduced that a proton is involved in the bridging group of the diamagnetic species, as first proposed by Thompson and Wilmarth.[3]

We have now carried out X-ray diffraction analyses of the two compounds. We find the green, paramagnetic compound to correspond to the formulation



I

as proposed by Werner[1] (except for the additional water of crystallization); however, the red, diamagnetic compound has the interesting arrangement



II

We report here the preliminary results of our investigations. Full details will be published elsewhere.

Crystals of the green compound, DL-$[(en)_2Co(O_2)(NH_2)Co(en)_2](NO_3)_4\cdot H_2O$ (I), were prepared by the method of Werner.[1] They are monoclinic, space group $P2_1/n$, with $a = 8.78$, $b = 23.97$, $c = 12.50$ A, $\beta = 95.8°$, $Z = 4$, $D_m = 1.72$, $D_x = 1.71$ g cm^{-3}. The intensities of 2812 independent reflections were estimated visually from Weissenberg photographs about a and c.

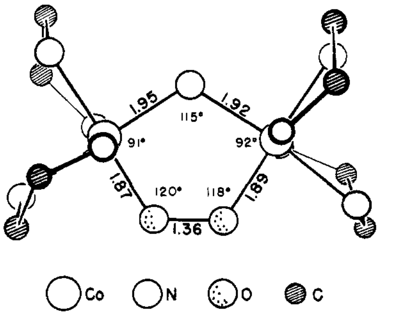


Figure 1. View of cation I down the a axis.

The red compound, DL-$[(en)_2Co(O_2H)(NH_2)Co(en)_2](NO_3)_4\cdot 2H_2O$ (II), was prepared by the method of Werner[1] and crystallized from saturated aqueous solution. The crystals are also monoclinic, space group $P2_1/n$, with $a = 8.23$, $b = 15.41$, $c = 20.48$ A, $\beta = 98.9°$, $Z = 4$, $D_m = 1.77$, $D_x = 1.79$ g cm^{-3}. The intensities of 2689 reflections were measured on an automated diffractometer using Fe Kα X radiation.

Both structures were solved by Patterson and electron-density methods and refined by least squares. At the present stage the R index for I is 0.087 and for II, 0.075.

The cation in the paramagnetic compound (I) is shown in Figure 1. The approximate planarity of the five-membered -Co-N-Co-O-O- ring and the length of the O-O bond, 1.36 ($\pm$0.03) A, suggest that the unpaired electron is concentrated in the O_2 bridge, which thus becomes a superoxo group; similar geometry has recently been found in a number of related compounds.[6-8]

The cation of II is shown in Figure 2. The three bonds to the briding oxygen atom are noncoplanar. The average of the Co-O-O angles is 115°; the O-O distance is about 1.42 A. The accuracy in our description of this portion of the structure is relatively low because of disorder within the crystals; apparently the nonbridging oxygen atom lies on one side of the four-membered -Co-N-Co-O- ring in about one-third of the molecules and on the other side in two-thirds of the molecules. We are collecting additional data in an attempt to improve the accuracy.

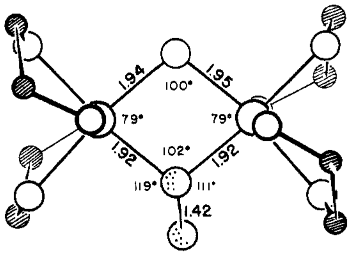


Figure 2. View of cation II down the a axis.

The coordination about the cobalt atoms in both compounds is approximately octahedral. All four ethylenediamine chelate groups within one cation have the same conformation (although one of the groups in I appears to be disordered). In both compounds (which are crystallized as the racemates) the conformations of the two optical isomers of each cation may be designated, using the symbols of Corey and Bailar,[9] as (kkkk) and (k'k'k'k'), respectively. We propose the name DL-μ-amido-μ-superoxo-bis{bis(ethylenediamine)cobalt(III)} tetranitrate monohydrate for I. For the O_2H group in II Mori and Weil[5] have already suggested the appropriate name "μ-hydroperoxo."

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Chemistry of Electron Transfer and Oxygen Transfer in Fused Salts[1]

Sir:

The oxygen electrode in molten alkali nitrate solvents has been the subject of significant controversies.[2-6] Recently, Inman[7] has reported (at an $O_2(Au)|O^{2-}$ electrode in a lithium–potassium chloride eutectic melt at 450°) a puzzling Nernstian slope of RT/F, in lieu of the expected $RT/2F$ for $2O^{2-} = O_2 + 4e$. We have substantiated polarographically a similar remarkable finding at Levich's rotated platinum disk electrode,[8] in solutions prepared by adding pure sodium oxide to a fused equimolar sodium–potassium nitrate solvent at 265°. Our results indicate conclusively the prevalence of the following oxygen-transfer (I) and electron-transfer (II) processes.

Oxygen transfer

$$NO_3^- + O^{2-} \longrightarrow NO_2^- + O_2^{2-} \qquad (I_1)$$

$$2NO_3^- + O_2^{2-} \rightleftharpoons 2NO_2^- + 2O_2^- \qquad (I_2)$$

Electron transfer

$$NO_2^- \rightleftharpoons NO_2 + e \qquad (II_1)$$

$$O_2^- \rightleftharpoons O_2 + e \qquad (II_2)$$

$$O_2^{2-} \rightleftharpoons O_2^- + e \qquad (II_3)$$

Because of reaction I_1, the ion O^{2-} cannot exist (at any appreciable concentration level) in equilibrium with nitrate melts. This is plausible in view of indications that in such media NO_3^- indeed exhibits the properties of a strong and reactive oxidant.[9]

The evidence on which our claim for the proposed reaction sequence rests is summarized in Figure 1 which is representative of an extensive series of experiments.

The steady-state current–voltage (c–v) curve shown in Figure 1 exhibits several sigmoid "waves," reminiscent of the shape of classical polarograms. Four well-defined limiting current domains (i) are evident. Their dependence on the angular velocity (ω) of the rotated disk indicator electrode was found to obey Levich's[8] applicable equations

$$i = (\text{constant})D^{2/3}\omega^{1/2}C \qquad (III)$$

$$i/D^{2/3} \propto C \text{ (when } \omega = \text{constant)} \qquad (IV)$$

where D and C denote respectively the diffusion coefficient and bulk concentration of the electroreactive (electrooxidizable or electroreducible) species. This concordance is an unequivocal diagnostic criterion indicating that our experimentally observed limiting currents were controlled by the rate of transport of the electroreactive species from the bulk of the melt to the electrode surface, under conditions of extreme concentration polarization.

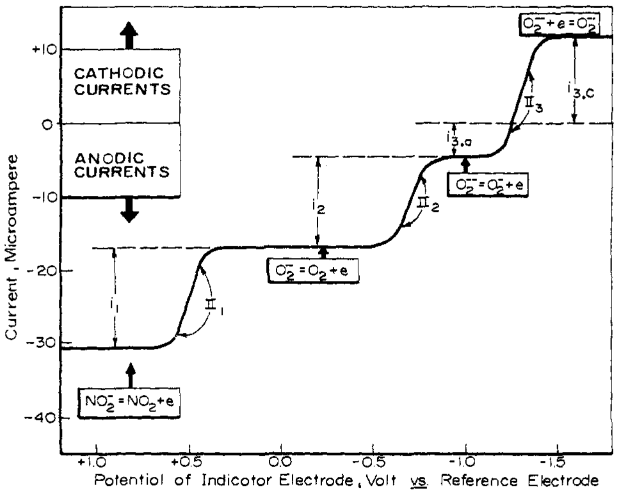

Figure 1. Typical current–voltage curve (corrected for residual currents, etc.) recorded at 265° in platinum-lined electrolysis cell: electrolyte, equimolar sodium–potassium nitrate, equilibrated with sodium oxide (1.10 mmoles of Na_2O per 1000 g of solvent); supernatant atmosphere, dry argon; indicator electrode, Levich's platinum disk, rotated at 600 rpm; reference electrode, $Ag|AgNO_3$(0.07 m in solvent melt). Potentials assigned in accordance with the Stockholm IUPAC Convention.

The anodic wave designated as II_1 in Figure 1 is readily identifiable in terms of its known half-wave potential and analytic geometry characteristics[3,5,10,11] with the electrooxidation of nitrite to NO_2 in accordance with eq II_1. The limiting current i_1 was proportional to the concentration of the ion NO_2^- in the bulk of the melt, as required by eq IV. We postulate the correspondence shown in Figure 1 between the other two c–v waves, on the one hand, and reactions II_2 (superoxide $\rightleftharpoons$ oxygen) and II_3 (peroxide $\rightleftharpoons$ superoxide) on the other hand. The rationale is outlined below.

II_3 is a composite wave whose anodic and cathodic limiting currents $i_{3,a}$ and $i_{3,c}$ were proportional to the bulk concentrations of peroxide (O_2^{2-}) and superoxide (O_2^-), respectively. The limiting current, i_2, of the anodic wave II_2 was also proportional to superoxide concentration. Quite generally on any given c–v curve

$$|i_{3,c}| = |i_2| \qquad (V)$$

These findings are uniquely consistent with the interpretations presented in Table I. It is apparent from the table that limiting currents i_2 and $i_{3,c}$ were due to the electrooxidation and electroreduction of the same

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