The Uptake of Oxygen by Aqueous Solutions containing Cobalt(II) Ions and Ethylenediamine

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The amount of oxygen taken up by aqueous solutions of various cobalt(II) salts containing ethylenediamine (en) attains a maximum for a stoicheiometric Co:en ratio of 1:3. In the products, isolated from the reaction mixture by the addition of alcohol, the Co:en ratio varies from 1:1·5 to 1:2·75.

DURING work on the oxygenation of organic compounds we investigated the absorption of oxygen by solutions of several cobalt(II) salts to which ethylenediamine (en) had been added.[1] Since our results differed from those obtained by other workers,[2] we repeated some of their experiments, and some of our own, but the discrepancy between our results and theirs remained.

RESULTS AND DISCUSSION

Aqueous cobalt(II) nitrate or perchlorate (4 mmol) was saturated by vigorous shaking with oxygen at 1 atm. Different amounts of ethylenediamine were then injected into the solutions and the subsequent oxygen uptake was recorded automatically. The presence of sodium nitrate or sodium perchlorate [2] decreased the oxygen uptake. The results are summarized in the Table.

Uptake of oxygen by cobalt(II) salt (4 mmol) in 50 ml water with different amounts of ethylenediamine at 23 °C

Mole ratio Co:en	1:2	1:2·5	1:3	1:3·5	1:5
Oxygen uptake in mmol by:					
$Co(NO_3)_2$	1·60	1·88	2·04	2·04	
$Co(ClO_4)_2$	1·48	1·80	2·00	2·04	1·90
$Co(NO_3)_2$ + 50 mmol $NaNO_3$	1·52	1·80	2·00	2·00	
$Co(ClO_4)_2$ + 50 mmol $NaClO_4$	1·40	1·68	1·96	2·00	
Results of Miller *et al.*[2] with $Co(ClO_4)_2$ + $NaClO_4$	1·56	2·00	2·00		

Oxygen uptake increases with increasing amounts of en to a maximum at a Co : en ratio of 1 : 3 (corresponding to a binuclear complex containing O_2). This disagrees with previously reported results,[2] which showed a maximum uptake at Co : en ratio of 1 : 2·5. Our results are confirmed by the u.v. spectra of the solutions (see the Figure). A similar result was obtained with a ten-fold increase in the concentrations of cobalt(II) salts and en.

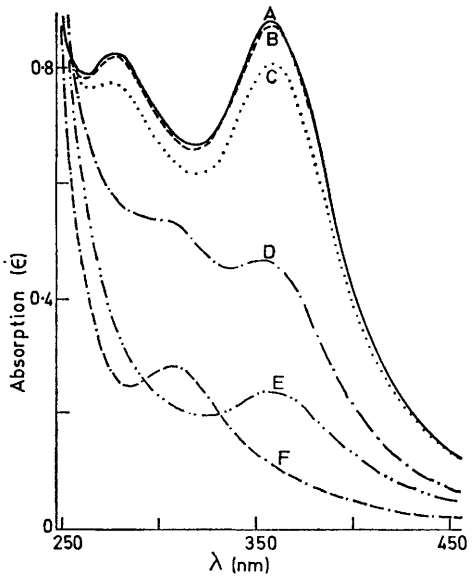
The reaction products, isolated from oxygenated solutions of cobalt(II) nitrate and perchlorate, where the ratio Co : en varies from 1 : 1 to 1 : 3, are mixtures in which the Co : en ratio varies from 1 : 1·5 to 1 : 2·5.

The u.v. spectrum of the reaction product obtained from a solution containing cobalt(II) and en in the 1 : 1 ratio corresponds not to an oxygen-containing binuclear complex, but most closely to an isomeric basic cobalt(III) salt co-ordinated with en. Similar spectra are obtained from equimolar mixtures of cobalt(III) salts with en and alkali.

[1] TNO Report CL 67/53, June 27, 1967.
[2] S. W. Foong, J. D. Miller, and F. D. Oliver, *J. Chem. Soc.* (*A*), 1969, 2847.

Therefore, it is clear that, when cobalt(II) salts are mixed with en in a 1 : 3 ratio (the en being added in three equal portions and the solution being shaken thoroughly in the presence of oxygen after each addition), there will be no oxygen uptake after addition of the third portion of the en since cobalt(II) ions are by then absent.

Even when the reaction was performed under an atmosphere of nitrogen, using a ratio of Co : en of 1 : 3 a small amount of an oxygen-containing complex was still formed (see Figure) owing to the presence of traces of oxygen. Consequently, for the preparation of the oxygen-containing cobalt(III) complexes it is necessary first to add the en and next to mix thoroughly before shaking with oxygen.



Absorption spectra of cobalt(II) nitrate solutions ($1·6 \times 10^{-3}$M) containing amounts of en in ratios of Co : en; A (1 : 3·5), B (1 : 3), C (1 : 2·5), D (1 : 2), E (1 : 3), and F (1 : 1). E was under nitrogen, the others were under oxygen

The concentrated oxygen-containing solutions of cobalt(II) salts and en are unstable. After several days at room temperature $Co(en)_3(NO_3)_3$ is isolated from the cobalt(II) nitrate solution.

An oxygenated solution of cobalt(II) perchlorate and en (Co : en = 1 : 5), when poured into alcohol, yields a product in which the Co : en ratio is 1 : 2·75. The same solution without addition of alcohol, when set aside for several weeks, spontaneously deposits dark brown crystals of a product containing Co and en in a 1 : 3 ratio.

Its analysis agrees with the values calculated for $Co_2(en)_6(O_2)(ClO_4)_4$. It is the only compound of the series in which the Co : en ratio is as high as 1 : 3. It shows an absorption maximum at 357 nm. The compound $Co(en)_3(OH)(ClO_4)_2$ gives practically the same analytical figures, but has an absorption maximum at a shorter wavelength.

EXPERIMENTAL

Isolation of $Co(en)_3(NO_3)_3$ *from Cobalt*(II) *Nitrate and Ethylenediamine*.—Cobalt(II) nitrate (11·6 g, 40 mmol), en (7·3 g, 120 mmol), and water (50 ml) were shaken thoroughly under oxygen at 1 atm. The oxygen uptake was 480 ml (19·2 mmol). At the end of the reaction, a small amount of gas was released (13 ml). [At 0 °C the uptake of oxygen was 500 ml (20 mmol).] After several days at room temperature, the solution deposited a red-brown product (4·0 g) [Found: C, 16·8; H, 5·7; Co, 13·9; N, 29·3. Calc. for $Co(en)_3(NO_3)_3$: C, 17·0; H, 5·7; Co, 13·9; N, 29·6%]. In agreement with earlier results [3] two absorption maxima were found: ε_{337} 87, ε_{467} 90·3. From cobalt(II) nitrate (11·6 g, 40 mmol) and en (6·0 g, 100 mmol), ratio of Co:en = 1 : 2·5, after the uptake of 370 ml (15 mmol) of oxygen, only 2·0 g of $Co(en)_3(NO_3)_3$ were isolated.

μ-*Peroxo-hexaethylenediaminedicobalt*(III) *Perchlorate*.—Cobalt(II) perchlorate (14·6 g, 40 mmol), and en (12·0 g, 200 mmol) and water (36 ml) were shaken at room temperature under oxygen at 1 atm. The uptake was 435 ml (17·5 mmol). The clear, dark red solution, after some weeks, deposited dark brown crystals (3·2 g) (Found: C, 15·9; H, 5·5; Cl, 16·1; Co, 13·1; N, 18·6. Calc. for $Co_2(en)_6(O_2)(ClO_4)_4$: C, 15·9; H, 5·3; Cl, 15·6; Co, 13·0; N, 18·5%). An absorption maximum was found at 357 nm.

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[3] M. Linhard, *Z. Elektrochem.*, 1944, **50**, 224, 237.