Sodium [*NN'*-Ethylenebis(salicylideneiminato)cobaltate(I)], a Reversible Carbon Dioxide Carrier

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Summary The reaction of sodium [*NN'*-ethylenebis(salicylideneiminato)cobaltate(I)] with carbon dioxide in both tetrahydrofuran and pyridine gave the reversible adducts: Co(salen)CO_2Na and (py)Co(salen)CO_2Na, respectively, containing CO_2 as the reduced species and in bent form.

An important property of metal chelates is their carrying ability towards simple molecules such as O_2 and CO,[1] and this aspect of their chemistry is emphasised by its analogy with that of transition-metal-containing enzymes.[2] Information on carbon dioxide fixation by metal complexes is very limited[3] especially for transition-metal chelates.[4]

We describe the reaction of CO_2 with Co(salen)Na, (I) [salen = *NN'*-ethylenebis(salicylideneiminato)], obtained by controlled reduction of the corresponding cobalt(II) compound, Co(salen), with sodium.[5]

The green solution of (I) in tetrahydrofuran (THF) absorbed 1 mol of CO_2 per cobalt atom in a few minutes at room temperature giving a brown solid insoluble in THF.

$$\underset{\text{(I)}}{\text{Co(salen)Na}} + CO_2 \overset{\text{THF}}{\rightleftharpoons} \underset{\text{(II)}}{\text{Co(salen)}CO_2\text{Na}} \qquad (1)$$

The suspension so obtained lost CO_2 *in vacuo* at room temperature in a few minutes, reverting to the green solution of (I); this absorption-desorption cycle can be repeated several times, and can also be observed in the solid state. Attempts to dissolve (II) in various solvents, not saturated with CO_2, resulted in the formation of the green solution of (I) and CO_2 evolution. Complex (II) gave satisfactory analytical data; its i.r. spectrum (Nujol), compared with that of Co(salen) or Co(salen)Na, showed three additional strong bands at 1680, 1278, and 1213 cm^{-1} (co-ordinated CO_2). Magnetic measurements on (II) gave no well reproducible values, owing to its sensitivity to hydrolysis, oxidation, and loss of CO_2, but nevertheless were in accord with a fundamentally diamagnetic complex. Decomposition of (II) in dilute H_2SO_4 gave 1 mol of CO_2, as did the reaction with benzyl chloride.

A reaction similar to (1) can be carried out in pyridine (py) with absorption of 1 mol of CO_2 per cobalt atom, to

$$\underset{\text{(I)}}{\text{Co(salen)Na}} + CO_2 \overset{\text{py}}{\rightleftharpoons} \underset{\text{(III)}}{\text{(py)Co(salen)}CO_2\text{Na}} \qquad (2)$$

afford red microcrystals of (III), decomposition of which in dilute H_2SO_4 or reaction with benzoyl chloride gave 1 mol of CO_2. A suspension of (III) in pyridine also gave a green solution of (I) *in vacuo*, although not so readily as (II). Complex (III) is diamagnetic ($\chi_M^{corr} = 315 \times 10^{-6}$ c.g.s.u. at 293 K) and gave satisfactory analytical data; its i.r. spectrum (Nujol) compared with that of Co(salen)(py) showed three additional strong bands at 1700, 1273, and 1208 cm^{-1}. It can be dried *in vacuo* without significant loss of CO_2. The stabilisation of the CO_2 complex (III) by the axial ligand pyridine is reminiscent of the same effect observed in dioxygen complexes.[6] The i.r. spectrum suggests that in both (II) and (III) CO_2 is co-ordinated as the reduced species and in the bent form.[7]. Beside this, it is impossible to say anything about the molecular arrangement in (II) and (III), which may be determined principally by the co-ordination sphere of the sodium cation, to which the CO_2 and salen oxygen atoms can contribute. The formation of a complex between metal chelates, oxygen atoms and alkali ions has been reported recently.[8,9]

It is generally accepted that CO_2 fixation involves[10] concerted attack of a base on the CO_2 carbon atom together with co-ordination of the oxygen to a 'hard' metal ion. In our case it is possible that the sodium cation acts as a Lewis acid in a concerted acid–base attack on CO_2 with cobalt(I) as the other partner.

Studies on naturally occurring CO_2 complexes indicate that care should be taken in predicting the course of CO_2 attack on metal chelates[11]. However, if we exclude the unlikely insertion of CO_2 in between, *e.g.*, the Co–O bond in the rather rigid chelate structure, it seems reasonable that the electrophilic carbon atom of CO_2[10] will prefer attachment to the cobalt(I) atom in Co(salen)Na, as a centre of maximum nucleophilicity.[12]

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