

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

By CARLO FLORIANI* and GIUSEPPE FACHINETTI

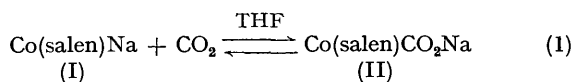
(Istituto di Chimica Generale ed Inorganica, Università di Pisa, 56100 Pisa, Italy)

Summary The reaction of sodium [*NN'*-ethylenebis(salicylideneiminato)cobaltate(I)] with carbon dioxide in both tetrahydrofuran and pyridine gave the reversible adducts: Co(salen)CO₂Na and (py)Co(salen)CO₂Na, respectively, containing CO₂ as the reduced species and in bent form.

An important property of metal chelates is their carrying ability towards simple molecules such as O₂ 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 limited³ especially for transition-metal chelates.⁴

We describe the reaction of CO₂ with Co(salen)Na, (I) [salen = *NN'*-ethylenebis(salicylideneiminato)], obtained by controlled reduction of the corresponding cobalt(II) compound, Co(salen), with sodium.⁵

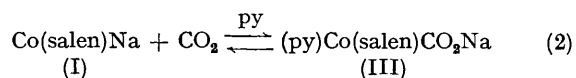
The green solution of (I) in tetrahydrofuran (THF) absorbed 1 mol of CO₂ per cobalt atom in a few minutes at room temperature giving a brown solid insoluble in THF.



The suspension so obtained lost CO₂ *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 CO₂, resulted in the formation of the green solution of (I) and CO₂ 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 CO₂). Magnetic measurements on (II) gave no well reproducible values, owing to its sensitivity to hydrolysis, oxidation, and loss of CO₂, but nevertheless were in accord with a fundamentally diamagnetic complex. Decomposition of (II) in dilute H₂SO₄ gave 1 mol of CO₂, 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 CO₂ per cobalt atom, to



afford red microcrystals of (III), decomposition of which in dilute H₂SO₄ or reaction with benzoyl chloride gave 1 mol of CO₂. 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 ($\chi_{\text{M}}^{\text{cor}} = 315 \times 10^{-6}$ 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 CO₂. The stabilisation of the CO₂ 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) CO₂ 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 CO₂ 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 CO₂ fixation involves¹⁰ concerted attack of a base on the CO₂ 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 CO₂ with

cobalt(I) as the other partner.

Studies on naturally occurring CO₂ complexes indicate that care should be taken in predicting the course of CO₂ attack on metal chelates¹¹. However, if we exclude the unlikely insertion of CO₂ in between, *e.g.*, the Co-O bond in the rather rigid chelate structure, it seems reasonable that the electrophilic carbon atom of CO₂¹⁰ will prefer attachment to the cobalt(I) atom in Co(salen)Na, as a centre of maximum nucleophilicity.¹²

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