

X-Ray Structure of the Reversible Dioxygen Adduct of [N,N'-(3,3'-Dipropylmethylamine)bis(salicylideneaminato)cobalt(II)]: Unusual Presence of both Dioxygenated and Non-dioxygenated Complex Molecules in the Crystal

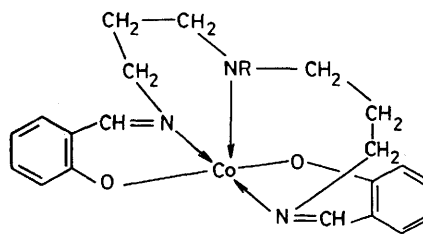
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Summary The crystal structure of the reversible dioxygen adduct of [N,N'-(3,3'-dipropylmethylamine)bis(salicylideneaminato)cobalt(II)] (**1**), crystallized from benzene, shows the presence of both dioxygenated and non-dioxygenated monomeric molecules containing, respectively, low-spin octahedral and high-spin five-co-ordinated cobalt atoms.

THE study of compounds capable of reversibly binding molecular oxygen has aroused great interest in recent years. However, the number of crystal structure determinations reported for these compounds is limited owing to the instability of the compounds and to difficulties in getting crystals suitable for X-ray analysis.¹ The isolation

and characterization of a reversible dioxygen adduct of (**1a**) has been recently reported.² On the basis of chemical



(1)

a; R = Me; [Co(salmdpt)]
b; R = H; [Co(saldpt)]

analysis the compound was assigned the formula $[\text{Co}(\text{saldpt})_2 \cdot \text{O}_2 \cdot 2\text{C}_6\text{H}_6]$ (**2**) which seemed to suggest a μ -peroxy-bridged dimeric structure of the type found for the unmethylated derivative $[\text{Co}(\text{saldpt})_2 \cdot \text{O}_2 \cdot \text{PhMe}]^3$ (**1b**). However, its deoxygenating behaviour and its magnetic and spectral properties suggested the presence in the solid of a cobalt(III) superoxo-compound weakly associated with a high-spin cobalt(II) complex. Evidence for some sort of interaction between the two complex molecules came from a low-temperature magnetic investigation which showed no spin-state change for (**2**), in contrast with the behaviour of the starting compound (**1a**), which showed spin pairing to occur at 15 K.² This seemed to exclude the presence of discrete molecules of the high spin starting complex.

Very small crystals of compound (**2**) were deposited during the oxygenation of a benzene solution of (**1a**). They were stable at room temperature in the air during the data collection, but extensive twinning complicated the choice of a crystal suitable for investigation.

Crystal data: $\text{C}_{54}\text{H}_{62}\text{Co}_2\text{N}_6\text{O}_6$, $M = 1009.0$; triclinic, space group $P\bar{1}$, $a = 17.045(4)$, $b = 12.697(3)$, $c = 11.668(3)$ Å, $\alpha = 94.23(3)$, $\beta = 90.06(3)$, $\gamma = 100.43(3)^\circ$; $Z = 2$, $D_c = 1.35$ g cm⁻³; $\mu(\text{Mo-K}\alpha) = 7.57$ cm⁻¹; $R = 0.088$, $R_w = 0.094$ for 1482 independent reflections with $F \geq 2.5\sigma(F)$.†

The crystal structure of (**2**) comprises two different types of molecule in a 1:1 ratio: type A (Figure 1), which can be

formally described as a Co^{III} superoxo complex, contains low-spin octahedral cobalt atoms, five co-ordinating positions being occupied by the donor atoms of the pentadentate ligand *saldpt* and the sixth position by a dioxygen molecule, bound in a bent end-on fashion;¹ the molecule of type B (Figure 2) does not contain co-ordinated dioxygen, but shows the presence of five-co-ordinated high-spin cobalt(II) atoms, the five donor atoms of the ligand forming an almost regular trigonal bipyramid. No apparent interaction was noted between the two molecules, the intermolecular distances all being normal. The shortest $\text{Co(A)} \cdots \text{Co(B)}$ distance is 7.54 Å.

As found in other cases,^{4,5} the dioxygen molecule shows a twofold statistical disorder, the O(3)-O(4)-O(4') plane almost bisecting the N(1)-Co-O(2) and N(2)-Co-O(1) angles. The dioxygen O-O distance [average 1.06(5) Å] is unrealistically too short, being even shorter than the O-O separation of 1.216 Å in molecular oxygen.⁶ A correction for the effect of the thermal motion and a small off-axis displacement of the co-ordinated oxygen atom would lead to a more reasonable bond length and a smaller Co-O-O angle. Coupling between the oxygen atom parameters made this model impracticable for the least-squares refinement.

The benzene molecules fill empty spaces in the crystal lattice; two of them, in close proximity to the co-ordinated dioxygen, appear to contribute to the formation of a hydrophobic pocket around it.

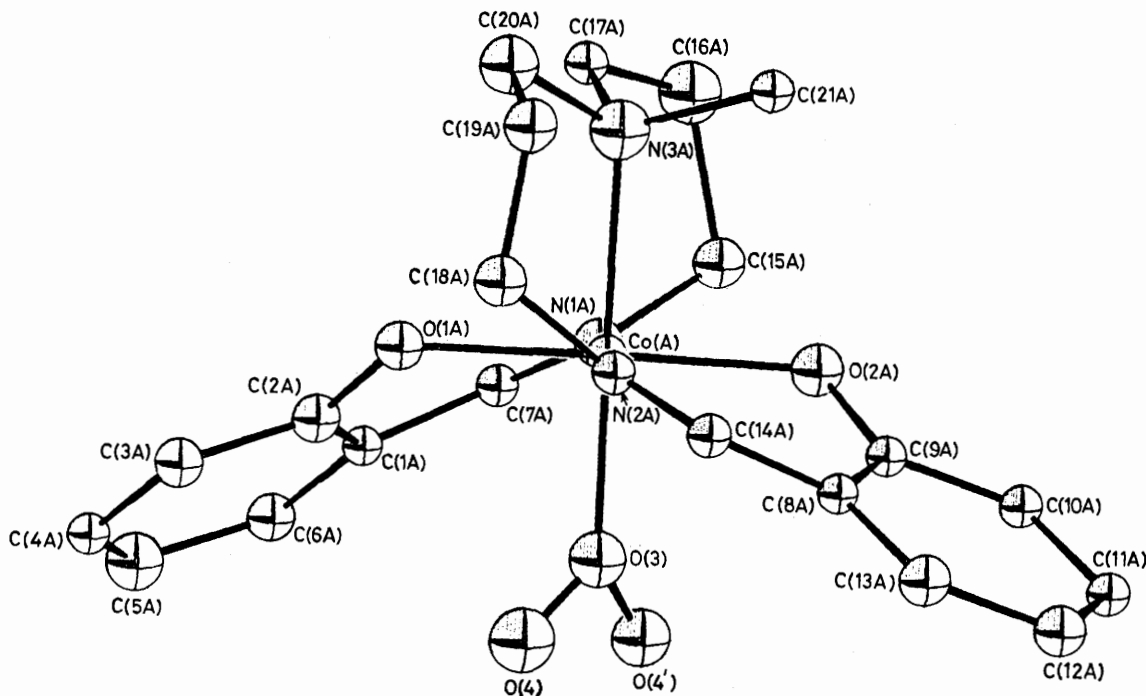


FIGURE 1. ORTEP drawing of the dioxygenated molecule (**2A**), showing the twofold orientational disorder of the dioxygen molecule. Selected bond lengths (Å) and angles ($^\circ$) are: Co-O(1) 1.91(2), Co-O(2) 1.93(2), Co-O(3) 1.88(2), Co-N(1) 1.90(2), Co-N(2) 2.00(2), Co-N(3) 2.09(3), $\angle \text{O(1)-Co-O(2)}$ 177(1), O(1)-Co-N(3) 91(1), O(2)-Co-N(3) 91(1), O(3)-Co-N(3) 179(1), N(1)-Co-N(2) 178(1), Co-O(3)-O(4) 137(4), Co-O(3)-O(4') 133(4).

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

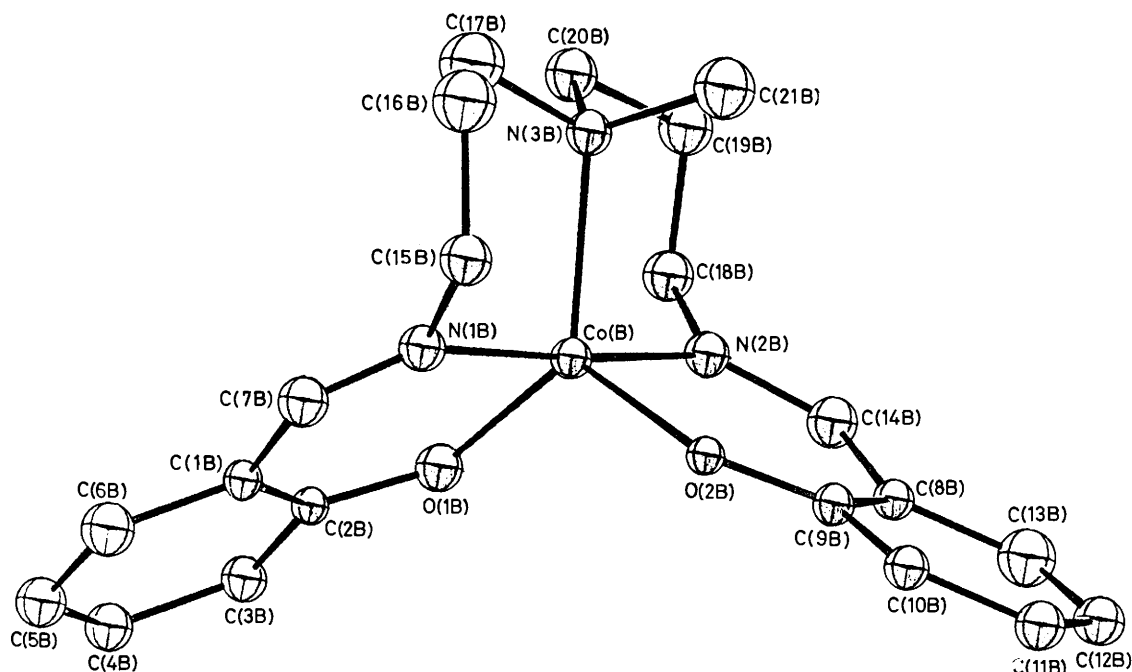


FIGURE 2. ORTEP drawing of the non-dioxygenated molecule (**2B**). Selected bond lengths (Å) and angles (°) are: Co–O(1) 2.01(2), Co–O(2) 1.97(2), Co–N(1) 2.03(2), Co–N(2) 2.02(2), Co–N(3) 2.16(2), \angle O(1)–Co–O(2) 120(1), O(1)–Co–N(3) 124(1), O(2)–Co–N(3) 114(1), N(1)–Co–N(2) 174(1).

The presence of discrete molecules of the high-spin precursor complex leaves unsolved the question of the different magnetic behaviour of (**2**) in comparison with that of (**1**),² the shortest Co(B) \cdots O(4) and Co(B) \cdots O(4') distances of 6.27 and 6.14 Å, respectively, being too long to allow even a weak interaction between the dioxygen moiety and the high-spin cobalt atom. It should be pointed out, however, that deviations from the regular

trigonal bipyramidal geometry in the precursor towards a square pyramid would favour spin pairing as reported for other five-co-ordinated cobalt complexes.⁷ However, this interpretation must await the X-ray structure investigation of the precursor (**1a**), which is currently in progress in our laboratory.

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