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The Crystal and Molecular Structure of a Cobalt(III) Compound of the Quadridentate Ligand N,N'-*o*-Phenylenebis(salicylideneiminate) in a Strained Non-Planar Configuration

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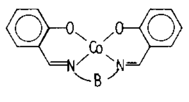
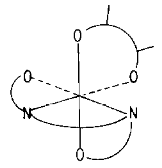
[Co(salen)] {I for B = $\cdot CH_2 \cdot CH_2 \cdot$} reacts with O_2 and β-diketonates[1,2], α-ketoacetic esters,[3] ω-nitroacetophenone[2] and malonic esters[3] to give cobalt(III) compounds of type II, in which the quadridentate ligand has a strained[4] non-planar configuration. These conditions produce cobalt–carbon bonded species with other potential carbanions, such as acetonitriles and mono-substituted acetylenes,[5] but no evidence could be obtained for this alternative bonding mode of the β-diketonates, *etc.*



(I)



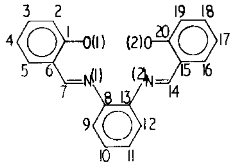
(II)

By contrast, the more rigidly planar quadridentate ligand in [Co(salph)] (I, B = o-C_6H_4) should favour C-bonding over the O,O-bidentate mode. This is marginally true. Compounds with [Co(salph)] are less easily prepared, but we have obtained [Co(salph)(L)] (where L = the monoanion of dibenzoylmethane, 3-(2-thenoyl)1,1,1-trifluoroacetone, ethylacetoacetate, or diethylmalonic ester). Their i.r. spectra prove that the last two compounds are indeed C-bonded (free carbonyls), but that the two β-diketonate compounds have the same structure II as their salen analogues.[4,6]

The dibenzoylmethanide compound [$C_{35}H_{25}CoN_2O_4$] gave orange–brown crystals from methanol. Monoclinic ($P2_1/n$), a = 16.89(1), b = 16.47(1), c = 9.84(1), β = 90.85(5), D_m = 1.440, D_c = 1.446, Z = 4. 3091 independent reflections were obtained on a Stoe 'Stadi 2' 2-circle automatic diffractometer (MoK_α with a graphite monochromator). The structure was solved by Patterson and Fourier techniques, and refined by block-diagonal least-squares to R = 0.076 using anisotropic thermal parameters for the cobalt, and isotropic ones for all other non-hydrogen atoms.

The structure is of type II and closely parallels those of [Co(salen)(L)] {L = acac[6] and bzac[4]}; but here the Co–O bond lengths involving the quadridentate are significantly different, with that of the out-of-plane salicylidene moiety being longer than normal {1.921(5) Å, *cf.* 1.877(5) Å to the other sal oxygen}. This reflects the greater strain required to force the salph ligand into the non-planar configuration. Such strain is taken up largely in a number of angular distortions of the *o*-phenylene and the out-of-plane salicylaldimine moieties (Table).

TABLE. Selected Bond Angles in the Quadridentate Ligand (°). The atoms O(1), N(1) and N(2) are co-planar with the cobalt.



O(1)–C(1)–C(6)	124.5	C(15)–C(20)–O(2)	123.9
C(1)–C(6)–C(7)	123.5	C(14)–C(15)–C(20)	118.5
C(6)–C(7)–N(1)	124.3	N(2)–C(14)–C(15)	121.2
C(7)–N(1)–C(8)	121.8	C(13)–N(2)–C(14)	121.8
N(1)–C(8)–C(13)	114.4	C(8)–C(13)–N(2)	112.5

Bond angles in the in-plane salicylaldimine are normal as are all bond-lengths within the quadridentate.

Clearly chelating ligands can adopt what may appear to be quite a strained configuration if the total bonding situation in the molecule requires it.

Acknowledgements

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