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Crystal and Molecular Structure of Two Oxygen-Inactive Forms of [N,N'-(3,3'-Dipropylmethylamine)bis(Salicylideneiminato) Cobalt(II)]

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The crystal and molecular structures of two oxygen-inactive forms of the title complexes, Co(salmedpt), have been determined by X-ray diffractometer data. One form crystallizing from benzene with one molecule of solvent per complex molecule, has the following unit-cell parameters: a = *26.205(5),* b = *14.684(3),* c = *12.815(3) Å, Z = 8, space group* Pcab. *Crystals of the other form obtained from acetone are monoclinic with* a = *20.842(4),* b = *13.842(3),* c = *6.795(2), β = 92.58(3) Å, Z = 4, space group* $P2_1/a$. *Both structures have been refined by conventional least-squares techniques to* R *factors of 0.069 (1177 unique reflections with* $I > 3\sigma$*) and 0.098 (2284 reflections) for the benzene adduct and the form from acetone respectively.*

The coordination geometry which is identical in both complexes, can be described as a slightly distorted trigonal bipyramid and is essentially similar to that of the deoxy Co(salmedpt) molecule in the dioxygen adduct $[Co(salmedpt)]_2 \cdot O_2 \cdot 2C_6H_6$.

Introduction

The isolation and characterization of a reversible dioxygen adduct of [N,N'-(3,3'-Dipropylmethylamine)bis(Salicylideneiminato) Cobalt(II)] having the chemical formula $[Co(salmedpt)]_2 \cdot O_2 \cdot 2C_6H_6$ has been reported [1]. On the basis of its deoxygenating behaviour and of its magnetic and spectral properties, the presence in the crystal of both low-spin octahedral cobalt(III) superoxo and high-spin five coordinate cobalt(II) precursor species was postulated [1]. A recent single crystal X-ray analysis on the compound has confirmed the existence of both dioxygenated and non-dioxygenated monomeric molecules [2].

In order to investigate the conformational changes which take place during the oxygenation process, we have attempted to determine the crystal structure of the precursor complex Co(salmedpt). Three different crystalline modifications of the compound were obtained: two from benzene, belonging to the monoclinic and orthorhombic systems, each one containing one molecule of benzene in the lattice, and a monoclinic form from acetone. Although all three modifications, when dissolved in benzene, reversibly adsorb oxygen, only the monoclinic one from benzene is oxygen-active in the solid state. We report here the detailed X-ray structural investigation of the two oxygen-inactive forms.

Experimental

The compounds were both prepared according to ref. 3. Recrystallization from acetone gave brown plate-like crystals. From benzene solutions the monoclinic form, less soluble, was first obtained as dark-brown prisms. After filtration, crystals of the orthorhombic form readily separated as well-formed dark red-brown prisms. Crystal data and data collection procedures are summarized in Table I.

The intensity data were corrected for Lorentz and polarisation effects. The intensities of three standard reflections were monitored periodically for stability control during data collection.

Both structures were solved by the heavy atom technique, with the use of Patterson and electron-density syntheses. Refinement was performed by means of the full-matrix least-squares method. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = a/(\sigma^2(F) + bF^2)$, where a and b are adjustable parameters.

The structure of the benzene adduct was refined with isotropic temperature factors for all the atoms except cobalt and its coordinating atoms, which were refined anisotropically. In order to reduce the number of parameters, rigid group refinement was used for the benzene ring of the solvent and of the salicylaldimine moieties. The hydrogen atoms bound to these atoms were also included in the group refinement.

The structure of the form from acetone was refined with anisotropic temperature factors for all the atoms. Hydrogen atoms were not included.

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TABLE I. Crystal Data and Data Collection.

Molecular formula	$C_{21}H_{25}N_3O_2Co \cdot C_6H_6$	$C_{21}H_{25}N_3O_2Co$
Formula weight	488.50	410.38
Crystal symmetry	orthorhombic	monoclinic
Space group	*Pcab*	$P2_1/a$
a, *b*, *c*, (A)	26.206(5), 14.684(3), 12.815(3)	20.842(4), 13.842(3). 6.795(2)
α, β, γ, (°)	90, 90, 90	90, 92.58(3), 90
$V(A^3)$	4931.3	1958.3
Z	8	4
D_c (g cm^{-3})	1.316	1.392
Crystal dimensions (mm)	~0.1 × 0.1 × 0.05	~0.1 × 0.1 × 0.05
μ (cm^{-1}) (Mok$_\alpha$, λ 0.7107 A)	7.54	9.34
Monochromatisation	Graphite monochromator	Graphite monochromator
Scan type	$\theta-2\theta$ symmetric	$\theta-2\theta$ symmetric
Scan width (°)	1.40	1.40
Scan speed (°/s)	0.05	0.05
Background time (s)	10	10
θ_{max} (°)	20.0	25.0
Number of unique intensities ($I > 3\sigma_I{}^a$)	1177	2284
Number of parameters refined	140	273
Final R, $R_w{}^b$	0.069; 0.085	0.098; 0.107

$^a\sigma(I) = [P + B_1 + B_2 + (0.01\ I)^2]^{1/2}$ where P is the total integrated peak count, B_1 and B_2 are the background counts, $I = P - (B_1 + B_2)$ and 0.01 I is an empirical correction for unrealistically small standard deviations in strong reflections. $^bR_w = [\Sigma_w (|F_o|-|F_c|)^2/\Sigma_w F_o^2]^{1/2}$.

TABLE II. Final Atomic Coordinates (×10^4) with Estimated Standard Deviations.

Atom	Co(salmedpt)·C_6H_6			Co(salmedpt) (from acetone)		
	x/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*
Co	1235(1)	5766(1)	7465(2)	2966(1)	38(1)	554(2)
O(1)	1122(3)	6376(7)	6114(6)	2469(3)	434(5)	2784(9)
O(2)	1372(3)	6349(6)	8805(6)	3198(4)	810(5)	−1688(10)
N(1)	455(3)	5752(6)	7712(7)	2123(4)	−361(7)	−922(12)
N(2)	2010(4)	5710(6)	7177(7)	3814(4)	430(6)	2024(11)
N(3)	1226(3)	4288(6)	7450(9)	3278(4)	−1432(6)	565(12)
C(1)	211(3)	6594(6)	6160(6)	1405(5)	345(7)	1354(16)
C(2)	691(3)	6710(6)	5711(6)	1857(5)	567(6)	2875(14)
C(3)	742(3)	7204(6)	4786(6)	1644(5)	989(7)	4676(15)
C(4)	312(3)	7581(6)	4311(6)	980(7)	1149(8)	4818(20)
C(5)	−168(3)	7465(6)	4760(6)	523(6)	948(10)	3292(23)
C(6)	−219(3)	6972(6)	5685(6)	756(6)	546(9)	1594(21)
C(7)	115(5)	6091(8)	7117(9)	1555(5)	−168(7)	−434(16)
C(8)	2288(3)	6524(5)	8711(6)	4110(5)	1680(7)	−214(17)
C(9)	1821(3)	6658(5)	9208(6)	3632(5)	1476(7)	−1760(16)
C(10)	1802(3)	7104(5)	10169(6)	3642(6)	2055(9)	−3550(19)
C(11)	2250(3)	7416(5)	10632(6)	4086(7)	2806(9)	−3690(25)
C(12)	2718(3)	7282(5)	10135(6)	4517(7)	3032(10)	−2136(29)
C(13)	2737(3)	6836(5)	9175(6)	4545(5)	2470(9)	−394(21)

(continued on facing page)

TABLE II. *(continued)*

Atom	Co(salmedpt)·C_6H_6			Co(salmedpt) (from acetone)		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
C(14)	2364(5)	6029(8)	7746(9)	4179(5)	1121(8)	1572(15)
C(15)	288(5)	5207(10)	8626(9)	2205(6)	−943(8)	−2703(16)
C(16)	353(5)	4187(11)	8397(11)	2438(7)	−1974(9)	−2101(18)
C(17)	661(9)	3940(17)	7460(20)	2714(12)	−2110(16)	−23(32)
C(17)'	972(12)	3898(20)	8358(25)	3191(19)	−1889(17)	−1401(44)
C(18)	2147(5)	5162(9)	6244(10)	3973(6)	−111(8)	3846(16)
C(19)	2085(6)	4138(11)	6483(12)	4150(7)	−1155(10)	3293(18)
C(20)	1460(11)	3910(19)	6506(21)	3562(15)	−1713(16)	2554(36)
C(20)'	1778(11)	3899(20)	7513(24)	3995(18)	−1513(21)	1209(49)
C(21)	1420(12)	3971(20)	8473(22)	3801(12)	−1565(17)	−984(33)
C(21)'	1023(12)	4003(19)	6366(22)	2834(18)	−1928(19)	2064(54)
C(1B)	−1393(4)	5673(7)	6677(7)			
C(2B)	−1187(4)	4797(7)	6651(7)			
C(3B)	−1082(4)	4339(7)	7580(7)			
C(4B)	−1182(4)	4757(7)	8536(7)			
C(5B)	−1388(4)	5633(7)	8562(7)			
C(6B)	−1493(4)	6091(7)	7633(7)			

In both structures two distinct sets of positions were refined for C(17), C(20) and C(21), owing to the presence of twofold orientational disorder about an axis collinear with the Co–N(3) bond direction. The refined occupancy factors of these atoms did not differ significantly from 0.5.

All the calculations were performed with the SHELX-76 set of programs [4] which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms taken from the International Tables [5].

Table II reports the list of the final atomic coordinates with estimated standard deviations obtained from the least squares inverse matrix. A Table of observed and calculated structure factors, as well as Tables of thermal parameters, complete bond lengths and angles, and least-squares plane equations, are available from the Editor.

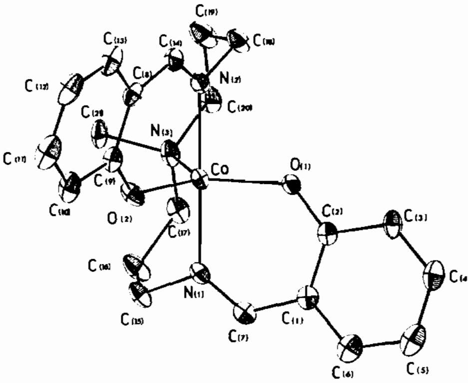

Fig. 1. ORTEP drawing of the molecule Co(salmedpt) showing the atom labelling. Ellipsoids enclose 30% probability. Atomic parameters for the drawing are from Co(salmedpt) from acetone.

Discussion

The structures of both forms of Co(salmedpt) consist of discrete molecules of the complex in which the cobalt atoms show a five-coordinate stereochemistry (Fig. 1). The coordination polyhedron can be described as a distorted trigonal bipyramid, with O(1), O(2) and N(3) in the equatorial plane and N(1) an N(2) in the axial positions. The cobalt atoms lie essentially in the equatorial planes. Table III reports bond lengths and angles in the molecules with estimated standard deviations. It can be noted that the values of the chemically analogous distances and angles in the two structures are identical within a few standard deviations, in spite of the different packing of the molecules in the crystal. This means that intermolecular forces are not particularly relevant in these crystals.

The distortion from the trigonal bipyramidal coordination geometry is mainly in the equatorial plane, with one of the angles, O(1)–Co–O(2), being

TABLE III. Selected Bond Distances (Å) and Angles (°) with Estimated Standard Deviations.

	Co(salmedpt)·C_6H_6	Co(salmedpt) from acetone		Co(salmedpt)·C_6H_6	Co(salmedpt) from acetone
Co–O(1)	1.971(9)	1.953(6)	Co–O(2)	1.952(8)	1.941(6)
Co–N(1)	2.069(9)	2.058(7)	Co–N(2)	2.064(10)	2.064(7)
Co–N(3)	2.170(9)	2.135(7)			
O(1)–C(2)	1.34(1)	1.29(1)	O(2)–C(9)	1.36(1)	1.29(1)
N(1)–C(7)	1.27(1)	1.27(1)	N(2)–C(14)	1.27(1)	1.27(1)
N(1)–C(15)	1.48(1)	1.47(1)	N(2)–C(18)	1.49(1)	1.47(1)
N(3)–C(17)	1.57(3)	1.55(2)	N(3)–C(17)′	1.46(3)	1.48(3)
N(3)–C(20)	1.46(3)	1.50(2)	N(3)–C(20)′	1.56(3)	1.54(3)
N(3)–C(21)	1.48(3)	1.56(2)	N(3)–C(21)′	1.55(3)	1.56(3)
O(1)–Co–O(2)	126.9(3)	127.9(3)	O(2)–Co–N(2)	89.7(4)	89.8(3)
N(1)–Co–N(2)	176.8(4)	179.6(2)	N(3)–Co–O(1)	116.4(4)	115.9(3)
O(1)–Co–N(1)	89.4(3)	89.0(3)	N(3)–Co–O(2)	116.6(4)	116.2(3)
O(1)–Co–N(2)	90.5(3)	91.3(3)	N(3)–Co–N(1)	88.9(4)	90.0(3)
O(2)–Co–N(1)	92.9(3)	90.2(3)	N(3)–Co–N(2)	88.3(4)	89.7(3)
Co–O(1)–C(2)	129.4(6)	129.5(5)	Co–O(2)–C(9)	129.6(6)	128.5(6)
Co–N(1)–C(7)	126.6(8)	127.0(6)	Co–N(2)–C(14)	126.9(8)	126.2(6)
Co–N(1)–C(15)	114.6(7)	114.9(6)	Co–N(2)–C(18)	113.8(7)	115.4(6)
C(7)–N(1)–C(15)	118.5(10)	118.2(8)	C(14)–N(2)–C(18)	119.0(10)	118.2(8)
Co–N(3)–C(17)	109.7(10)	110.9(9)	Co–N(3)–C(17)′	113.0(13)	112.3(11)
Co–N(3)–C(20)	112.4(12)	111.0(9)	Co–N(3)–C(20)′	110.8(12)	111.2(11)
Co–N(3)–C(21)	107.6(12)	109.4(8)	Co–N(3)–C(21)′	106.4(12)	103.4(11)

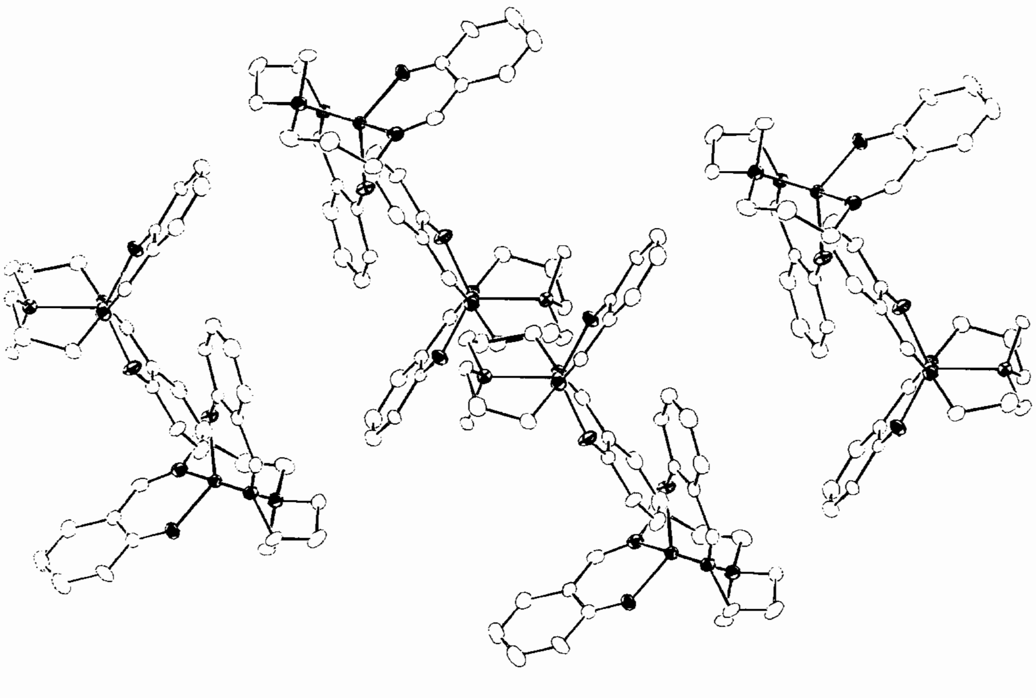

Fig. 2. Crystal packing of Co(salmedpt) from acetone. The view is approximately down the *x* axis.

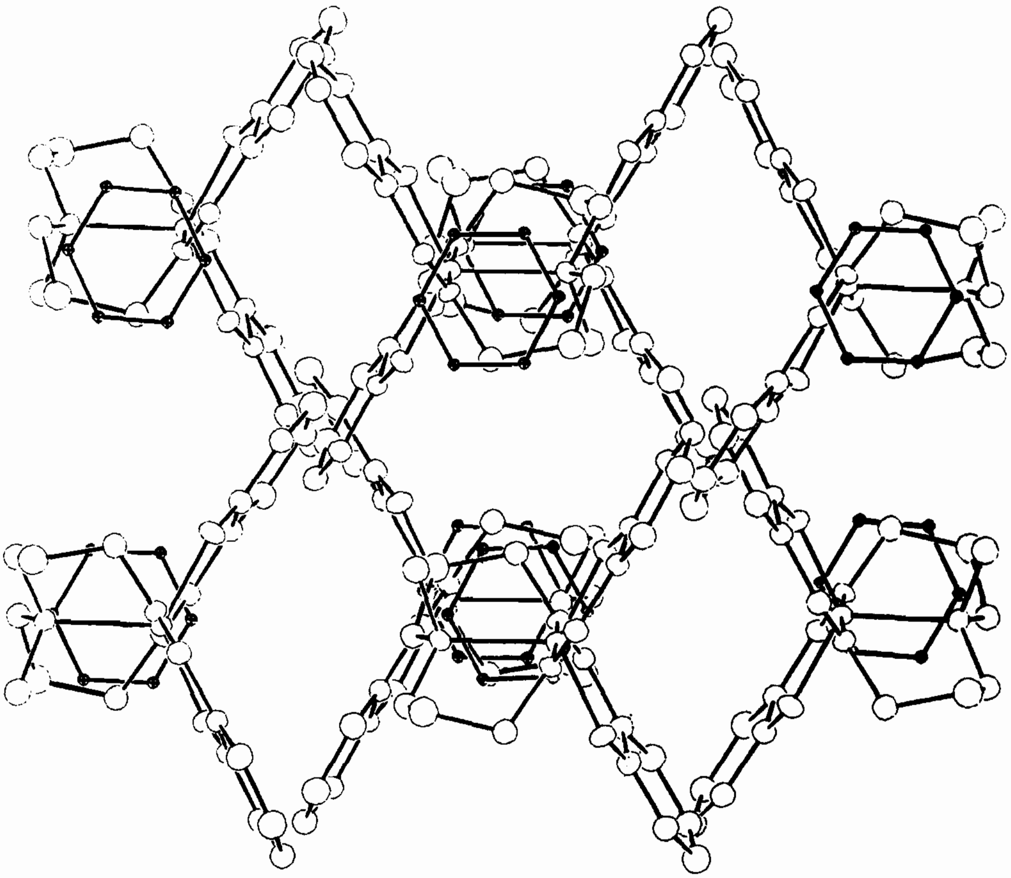

Fig. 3. Crystal packing of Co(salmedpt)·C_6H_6. The view is approximately down the x axis.

larger than the other two. This can be interpreted as a distortion of the complex molecules toward a square-pyramidal structure, whose stability is comparable with that of the trigonal bipyramid [6].

Both molecules show the presence of a non crystallographic twofold symmetry axis, colinear with the Co–N(3) bond direction. Twofold symmetry at N(3) is restored by a twofold orientational disorder of the molecules around the Co–N(3) bond direction.

The coordination geometry of the cobalt atoms is essentially similar to that found in the deoxy molecule of Co(salmedpt) in the crystal lattice of [Co(salmedpt)]$_2$·O_2·$2C_6H_6$, although the latter lacks the non-crystallographic twofold axis through Co–N(3). This rules out any interpretation of the different magnetic behaviour between oxygen adduct and precursor, based on different coordination geometries of the five-coordinate cobalt atoms [2]. It is also interesting to compare the stereochemistry about the cobalt atom with that about the nickel atom in the analogous Ni(salmedpt) and Ni(saldpt) [7, 8]. In these complexes the nickel atoms show a five-coordinated geometry essentially similar to that of the cobalt atom in the present compounds. This shows that in all these complexes the shape of the coordination polyhedron is mainly imposed by the steric constraints of the ligand molecule.

However a closer inspection of the angles about the metal atoms shows that the O–M–O angles in the nickel complexes are remarkably larger than in the cobalt compounds (140.6°(3) and 145.7°(2) against 126.9°(3) and 127.9°(3)). These differences cannot be attributed to packing forces, which, as noted above, are not particularly strong in this type of complexes.

Furthermore, inspection of the crystal data shows that Ni(salmedpt) and Co(salmedpt) from acetone are isomorphous and therefore crystal forces in the two compounds should have similar effects. Simple crystal field considerations in fact, show that for both cobalt(II) and nickel(II) in weak fields of D_{3h} symmetry, minimization of in plane ligand-d electrons repulsion is achieved by an increase of one of the equatorial angles of the coordination bipyramid

[9]. The widening must be larger for nickel(II) which has double occupancy of one of the in-plane orbitals.

It is interesting to note that, although the O(1)–Co–O(2) angles remain unchanged in the two compounds, the angle between the salicylaldimine planes is about 10° larger in the benzene adduct, being 118.2° and 108.3° respectively for the two compounds. This effect, which is most likely due to the presence of the benzene molecule in the crystal, is to be related with the important role played by the solvent in the formation of the dioxygen adduct [1].

Figures 2 and 3 show the crystal packing for both compounds. The question of the activity towards dioxygen in the solid state will probably be made clear by a comparison between the crystal packing of the three precursor forms with that of the dioxygen adduct. In fact, preliminary results from our laboratory show that the coordination geometry about the cobalt atom in the oxygen-active form is essentially similar to that of the inactive forms.

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