Crystal Structures of Bis[*N*-(3-methoxysalicylidene)isopropylaminato]nickel(II) (Brown Room Temperature Phase) and -cobalt(II)

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The crystal structures of two Schiff base complexes, bis[*N*-(3-methoxysalicylidene)isopropylaminato]nickel (II) and -cobalt(II), have been determined. Ni complex: brown, room temperature phase, monoclinic, $P2_1/c$, $a=21.089$, $b=7.254$, $c=14.386$ Å, $\beta=98.40°$, $Z=4$, final $R=0.076$. Co complex: red, triclinic, $P\bar{1}$, $a=22.699$, $b=7.395$, $c=14.099$ Å, $\alpha=107.78$, $\beta=99.03$, $\gamma=93.75°$, $Z=4$, final $R=0.13$. In both crystals the metal ions have distorted tetrahedral coordinations. The two crystals are roughly isostructural, although appreciable differences exist in both of the molecular and crystal structures. The Co complex gives a unique example of the methoxy group which sticks out nearly perpendicularly from the phenyl plane.

Recently Takeuchi and Yamada[1] isolated two stereochemical isomers of bis[*N*-(3-methoxysalicylidene) isopropylaminato]nickel(II). Brown and green crystals were obtained from methanol and ethylether solutions, respectively. In addition to these two crystalline forms, two other new high temperature forms, again brown and green ones, were found by Arai *et al.*[2] in their detailed studies on the thermal and magnetic properties of this complex. The spectroscopic and magnetic studies revealed that in both of the brown forms, room and high temperature ones, the molecular structures are almost the same and the central Ni ions are coordinated tetrahedrally, while in the two green forms the molecules have a square-planar coordination of Ni.[1,2]

The cobalt(II) complex of the same ligand was also prepared, and the Co ion was shown to have a tetrahedral coordination.[3] The unit cell dimension of the crystal is not so far from that of the brown Ni complex in the room temperature form. Thus it may be expected that these two crystals are isostructural with each other, although they are different in symmetry.

In this work, the crystal structures of the brown Ni complex in the room temperature form and of the Co complex were studied.

Table 1. Crystallographic data of (3-CH_3O-SAL·*i*-$C_3H_7)_2$M(II)

	Ni complex	Co complex	Cu complex
Color	Brown	Red	Red brown
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	21.089(2)	22.699(3)	10.329(1)
b	7.254(1)	7.395(2)	23.155(2)
c	14.386(1)	14.099(3)	9.188(1)
α (°)		107.78(2)	
β	98.40(1)	99.93(2)	96.04(1)
γ		93.75(2)	
V (Å^3)	2177.2	2202.2	2185.3
D_m (g/cm^3)	1.352	1.350	1.354
D_x	1.350	1.336	1.356
Z	4	4	4

Experimental

The crystallographic data of the brown room temperature form of bis[*N*-(3-methoxysalicylidene)isopropylaminato]-nickel(II) and those of the red Co complex are listed in Table 1. The data of the red brown crystal of the Cu complex with the same ligand[4] are also listed for comparison.

The X-ray intensity data were obtained on a four-circle diffractometer (Rigaku) with Zr-filtered Mo$K\alpha$ radiation. The 2θ-ω scan method was used, and the background counts were made at both scan limits. The maximum 2θ measured and numbers of non-zero reflections collected and used in the structure determinations are: 55° and 3845 for the Ni complex, and 45° and 3676 for the Co complex, respectively. The intensities were corrected for only Lp factors. The sizes of the crystals used were $0.5\times0.4\times0.2$ mm for the Ni complex, and $0.1\times0.1\times0.3$ mm for the Co complex.

Structure Determination

The structures were determined by the heavy atom Fourier method. The refinements were made by a block-diagonal least-squares calculations.[5] Unit weight was assigned for all the non-zero reflections. All the atomic scattering factors were taken from International Tables for X-Ray Crystallography, Vol. III.[6] For the metal ions the scattering factors of the univalent cations Co^+ and Ni^+ were used in consideration of the electroneutrality principle.[7] The computations were done on a NEAC 2200-700 of Osaka University and a FACOM 230-60 of Nagoya University.

Ni Complex: All the hydrogen atoms were included in the refinement. The final R is 0.076 for non-zero reflections.[8] The final parameters are listed in Tables 2 and 3. The bond distances and angles are shown in Fig. 1. The e.s.d.'s of the distances and angles among the non-hydrogen atoms are 0.004—0.014 Å and 0.2—0.8°, respectively. The ORTEP drawing[9] is shown in Fig. 2.

Co Complex: Two crystallographically independent molecules exist in the crystal. Anisotropic temperature factors were assigned to the Co atoms only, and the C, N and O atoms were refined with isotropic temperature factors. No hydrogen atoms were included in the calculation. The final R is 0.128.[8] No further

TABLE 2. Ni(3-CH_3O-SAL·*i*-C_3H_7)$_2$: THE ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS ($\times 10^4$)
Thermal parameters are in the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	2371(0)	6749(1)	1336(1)	16(0)	136(1)	46(0)	−9(1)	9(0)	−6(1)
C(1)	3721(3)	8639(7)	926(4)	19(1)	122(10)	47(3)	3(6)	14(3)	12(9)
C(2)	3593(2)	8549(7)	1860(4)	17(1)	104(10)	49(3)	3(5)	15(3)	0(9)
C(3)	4090(3)	9126(8)	2572(4)	19(1)	173(12)	48(3)	−9(7)	9(3)	16(10)
C(4)	4677(3)	9728(10)	2369(5)	19(1)	214(15)	67(4)	−18(8)	11(4)	6(13)
C(5)	4786(3)	9821(10)	1438(5)	20(1)	220(15)	78(5)	−3(8)	33(4)	24(14)
C(6)	4327(3)	9284(9)	739(5)	22(1)	204(14)	59(4)	6(7)	31(4)	12(12)
C(7)	3248(3)	8144(9)	132(4)	20(1)	212(13)	45(3)	11(8)	14(3)	36(11)
C(8)	2293(3)	7131(13)	−772(5)	28(1)	398(24)	46(4)	4(11)	−2(4)	−15(16)
C(9)	1752(4)	8534(16)	−902(6)	33(2)	521(34)	82(6)	26(15)	−10(6)	89(24)
C(10)	2028(4)	5172(15)	−834(6)	42(3)	494(32)	68(5)	−50(16)	−19(6)	−164(22)
C(11)	4391(4)	9729(12)	4200(5)	31(2)	327(21)	61(4)	−79(11)	−4(5)	−18(16)
N(1)	2695(2)	7420(7)	161(3)	22(1)	210(11)	43(3)	18(6)	10(3)	−7(9)
O(1)	3050(2)	7986(5)	2101(3)	17(1)	182(9)	42(2)	−25(5)	11(2)	−12(7)
O(2)	3931(2)	9040(7)	3463(3)	27(1)	298(12)	42(2)	−63(6)	5(3)	11(9)
C(21)	1231(3)	3822(8)	1609(4)	22(1)	178(12)	45(3)	−21(7)	13(3)	−7(10)
C(22)	1066(3)	5683(8)	1385(4)	17(1)	193(13)	38(3)	−23(6)	9(3)	−31(10)
C(23)	400(3)	6142(9)	1241(4)	20(1)	209(13)	42(3)	−24(7)	15(3)	−25(10)
C(24)	−53(3)	4825(10)	1372(5)	20(1)	282(18)	58(4)	−37(8)	8(4)	−39(14)
C(25)	120(3)	2999(10)	1610(5)	27(2)	258(17)	61(4)	−70(9)	19(4)	11(14)
C(26)	751(3)	2505(9)	1712(5)	27(2)	208(14)	51(4)	−38(8)	6(4)	21(12)
C(27)	1882(3)	3205(9)	1746(4)	26(2)	161(12)	50(3)	−2(8)	7(4)	−8(11)
C(28)	3008(3)	3120(9)	1932(5)	24(2)	146(12)	87(5)	33(8)	11(4)	17(13)
C(29)	3449(4)	3500(11)	1221(6)	28(2)	256(19)	114(7)	49(10)	33(6)	11(19)
C(30)	3314(4)	3651(13)	2905(6)	31(2)	335(24)	91(6)	58(12)	−19(6)	27(19)
C(31)	−402(3)	8408(12)	757(5)	21(2)	321(20)	67(4)	31(10)	13(4)	38(16)
N(2)	2396(2)	4115(7)	1685(4)	19(1)	158(10)	57(3)	7(6)	9(3)	−6(9)
O(3)	1481(2)	6980(6)	1296(3)	18(1)	167(9)	62(2)	17(5)	17(2)	4(8)
O(4)	265(2)	7920(6)	993(3)	19(1)	225(11)	76(3)	17(5)	12(3)	13(9)

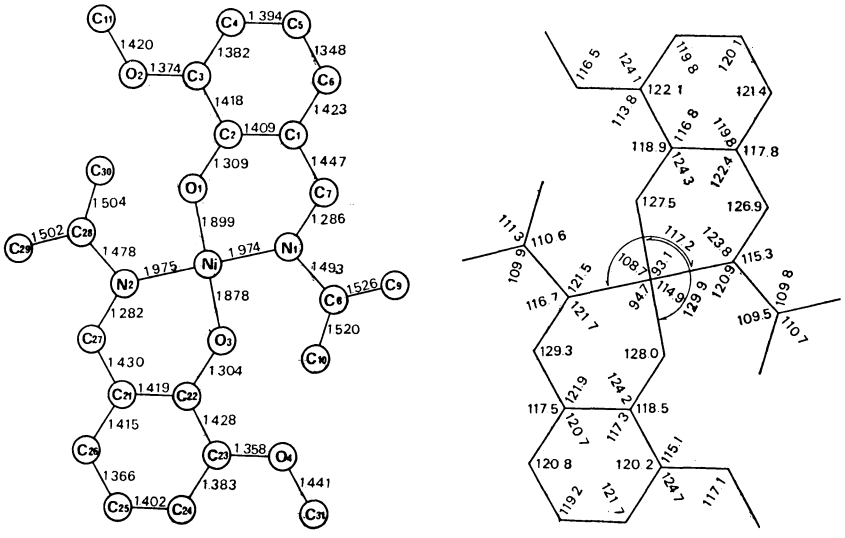

Fig. 1. Ni(3-CH_3O-SAL·*i*-C_3H_7)$_2$: bond distances and angles. The e.s.d.'s of the distances and angles among C, N, and O are 0.004—0.014 Å, and 0.2—0.8°, respectively.

refinements were attempted, because too much CPU time was needed, and also the higher accuracies seemed to be of less importance for this crystal. The parameters are listed in Table 4. The e.s.d.'s of the distances and angles are 0.01—0.035 Å and 0.5—2°, respectively. Only the mean values of the distances and angles of the chemically equivalent bonds are shown in Fig. 3. The ORTEP drawing is shown in Fig. 4.

Table 3. Ni(3-CH_3O-SAL·*i*-$C_3H_7)_2$: the positional parameters of the hydrogen atoms ($\times 10^3$)

	x	y	z		x	y	z
H(1)	500	1028	287	H(21)	−50	515	123
H(2)	523	1032	133	H(22)	−27	217	169
H(3)	435	934	0	H(23)	90	132	194
H(4)	340	839	−51	H(24)	192	190	188
H(5)	259	723	−134	H(25)	284	170	184
H(6)	145	837	−167	H(26)	321	316	61
H(7)	147	821	−34	H(27)	359	490	123
H(8)	193	973	−88	H(28)	380	277	130
H(9)	183	497	−141	H(29)	297	354	333
H(10)	246	435	−67	H(30)	336	479	302
H(11)	165	501	−19	H(31)	376	322	305
H(12)	452	1110	406	H(32)	−67	739	19
H(13)	417	967	479	H(33)	−63	826	130
H(14)	482	882	422	H(34)	−42	973	51

The average e. s. d. of the parameters is 0.075 Å.

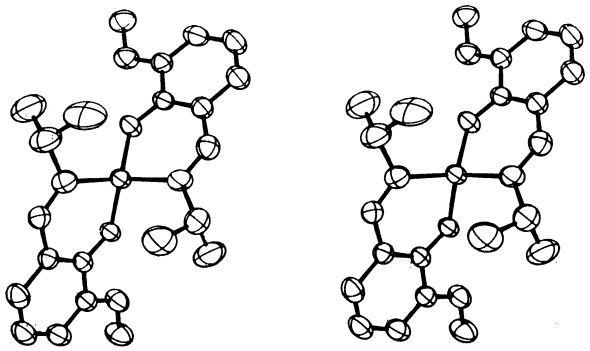

Fig. 2. Ni(3-CH_3O-SAL·*iso*-$C_3H_7)_2$: ORTEP drawing of a molecule, thermal ellipsoids are drawn at 50% probability level.

Table 4. Co(3-CH_3O-SAL·*i*-$C_3H_7)_2$: the atomic coordinates ($\times 10^4$), isotropic temperature factors ($Å^2 \times 10$) and their e. s. d.

	x	y	z	B		x	y	z	B
Molecule A					Molecule B				
Co(A)	1863(1)	223(3)	1253(2)	*	Co(B)	3289(1)	2246(3)	6510(2)	*
N(1A)	1628(5)	−1681(17)	−102(9)	37(3)	N(1B)	3533(6)	1783(18)	5190(10)	45(3)
O(1A)	2685(4)	−185(14)	1513(7)	40(2)	O(1B)	4028(5)	3767(14)	7296(8)	44(2)
O(2A)	3837(5)	−89(16)	2070(9)	54(3)	O(2B)	4964(6)	5633(18)	8654(10)	66(3)
C(1A)	2683(6)	−2305(21)	−176(11)	35(3)	C(1B)	4561(7)	3087(24)	5942(13)	48(4)
C(2A)	2974(6)	−1195(18)	815(10)	26(3)	C(2B)	4525(7)	3890(22)	6956(12)	41(3)
C(3A)	3593(7)	−1219(21)	1110(11)	37(3)	C(3B)	5052(7)	4915(23)	7673(12)	44(3)
C(4A)	3911(7)	−2217(23)	406(12)	44(3)	C(4B)	5614(9)	5105(30)	7388(16)	71(5)
C(5A)	3616(8)	−3372(24)	−562(13)	51(4)	C(5B)	5651(10)	4298(32)	6404(17)	76(5)
C(6A)	3006(7)	−3456(23)	−853(12)	43(3)	C(6B)	5147(10)	3257(32)	5643(17)	78(6)
C(7A)	2024(7)	−2533(22)	−571(12)	41(3)	C(7B)	4077(8)	2194(26)	5122(14)	57(4)
C(8A)	973(7)	−2270(24)	−699(13)	48(4)	C(8B)	3082(9)	1050(29)	4170(16)	68(5)
C(9A)	666(8)	−470(26)	−584(14)	55(4)	C(9B)	2648(12)	−574(39)	4197(21)	101(7)
C(10A)	668(11)	−3676(34)	−257(18)	83(6)	C(10B)	2727(10)	2647(31)	4058(17)	74(5)
C(11A)	4506(9)	32(28)	2401(15)	65(5)	C(11B)	5467(10)	6748(32)	9461(17)	77(5)
N(2A)	1770(5)	2986(17)	1412(9)	38(3)	N(2B)	3030(5)	102(17)	6949(9)	38(3)
O(3A)	1363(4)	9(14)	2186(7)	38(2)	O(3B)	2567(4)	3445(14)	6626(7)	39(2)
O(4A)	741(5)	−754(17)	3452(9)	59(3)	O(4B)	1613(5)	5539(16)	6683(8)	51(2)
C(21A)	998(6)	3100(20)	2430(11)	33(3)	C(21B)	2018(6)	1017(21)	7068(11)	36(3)
C(22A)	1027(6)	1305(20)	2594(11)	32(3)	C(22B)	2079(7)	2716(21)	6823(11)	37(3)
C(23A)	680(7)	949(23)	3258(12)	44(3)	C(23B)	1564(7)	3766(23)	6852(12)	46(4)
C(24A)	296(8)	2173(24)	3704(13)	50(4)	C(24B)	1036(8)	3125(25)	7066(13)	51(4)
C(25A)	257(8)	3890(27)	3482(14)	58(4)	C(25B)	999(8)	1430(25)	7295(13)	54(4)
C(26A)	597(7)	4359(23)	2875(12)	44(3)	C(26B)	1481(7)	393(24)	7282(13)	48(4)
C(27A)	1384(7)	3848(21)	1904(11)	36(3)	C(27B)	2510(6)	−157(20)	7157(11)	33(3)
C(28A)	2158(7)	4111(23)	1008(13)	47(4)	C(28B)	3450(8)	−1270(26)	7196(14)	54(4)
C(29A)	2229(9)	2898(30)	−67(16)	70(5)	C(29B)	3756(10)	−2007(32)	6288(17)	77(5)
C(30A)	2801(8)	4731(27)	1752(14)	59(4)	C(30B)	3927(10)	−142(31)	8156(16)	73(5)
C(31A)	774(12)	−838(39)	4430(21)	100(7)	C(31B)	1622(10)	5465(33)	5685(18)	81(6)

*Anisotropic temperature factors of Co ($\times 10^4$) in $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(A)	18(0)	184(5)	52(1)	20(3)	14(1)	50(4)
Co(B)	19(1)	200(5)	49(1)	11(3)	13(1)	47(4)

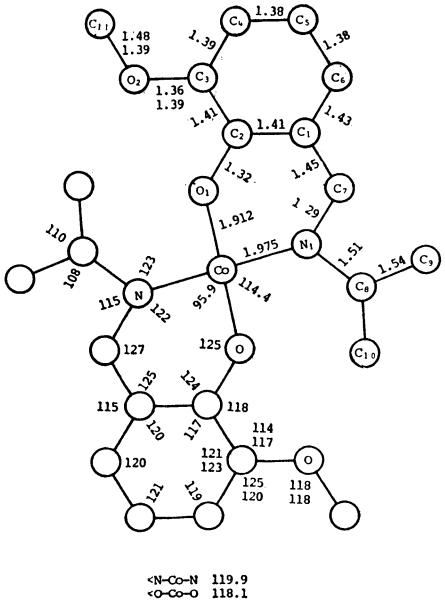

Fig. 3. Co(3-CH_3O-SAL·*i*-C_3H_7)$_2$: bond distances and angles. The mean values of the chemically equivalent bonds are shown. For the methoxy groups, the mean values in the planar methoxyphenyl groups (upper) and in the non-planar groups(lower) are shown.

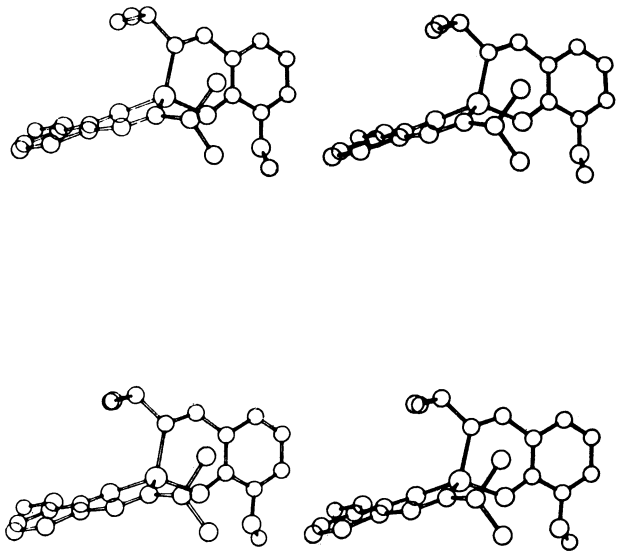

Fig. 4. Co(3-CH_3O-SAL·*i*-C_3H_7)$_2$: ORTEP drawing of molecules A (top) and B (bottom).

Molecular Structure

The molecular stucture of the present Ni complex, except for the methoxy group, is nearly identical with that of bis[*N*-isopropylsalicylaldiminato]nickel(II),[10] and no appreciable difference in the shapes and sizes is found between the two complexes. In the crystal of the Co complex two crystallographically independent molecules, A and B, have almost the same stucture, which bears also close resemblance to those of the two Ni complexes.

The tetrahedral coordination of the Ni(II) and Co(II) ions is thus confirmed. Although the distortions from the ideal tetrahedral form are large owing to the formations of the chelate rings, the distortion in the Co complex is a little smaller than that in the Ni complex. This finding agrees with the expectation of the simple crystal field theory.

Each molecule is characterized by several planar groups, of which details are listed in Tables 5 and 6. In any molecule two salicylideneamine planes intersect nearly at right angle with each other, the dihedral angles being 87, 87, and 79° for the Co(A), Co(B), and Ni complexes, respectively. The angle in bis-[*N*-isopropylsalicylaldiminato]nickel(II) is 82°.[10] The variation in the dihedral angles reflects the magnitudes of the distortions from the ideal tetrahedral coordi-

Table 5. Ni(3-CH_3O-SAL·*i*-C_3H_7)$_2$: Best planes
Planes I and II: each half of the molecule.
Planes III and IV: isopropyl groups.

(a) Equations* $lX+mY+nZ=p$

	l	*m*	*n*	*p*
I	0.3658	−0.9287	0.0610	−2.9432
II	0.0692	−0.2393	−0.9685	−2.7385
III	−0.1626	0.0013	0.9867	−1.8904
IV	−0.3664	0.9199	−0.1400	−0.4790

* $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$

(b) Dihedral angles (°)

	II	III	IV
I	79.1	90.0	4.6
II		14.7	83.7
III			85.6

(c) Displacements from planes (×10^3 Å)

Plane I		Plane II	
C (1)	3	C (21)	13
C (2)	−26	C (22)	−22
C (3)	−24	C (23)	3
C (4)	21	C (24)	−18
C (5)	33	C (25)	−7
C (6)	34	C (26)	28
C (7)	−36	C (27)	25
C (8)	−100	C (28)	−55
N (1)	25	N (2)	27
O (1)	−63	O (3)	−62
O (2)	−80	O (4)	19
Ni	239	Ni	52
C (11)*	−182	C (31)*	166

* Not included in the estimations of the equations.

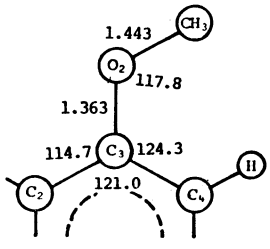

Fig. 5. The bond distances (Å) and angles (°) for the methoxy groups in the planar methoxyphenyl groups reported so far.

nation. The metal ions are slightly out of the chelate ring planes by 0.05—0.23 Å. The isopropyl group plane is nearly perpendicular to the chelate ring to which it is attached.

The phenyl groups show a common interesting feature, that is, the three C–C bonds nearest to the metal ion, C(1)–C(2), C(2)–C(3), C(1)–C(6) and their equivalents, are longer than the three farthest C–C bonds, C(3)–C(4), C(4)–C(5), C(5)–C(6) and their equivalents. This feature has been also found in several related compounds,[11] and may be explained by the presences of significant double bond characters in the exocylclic C(2)–O(1), C(1)–C(7) and their equivalents, although the shortenings of the farthest bonds may be partly due to the thermal vibration of the molecules.

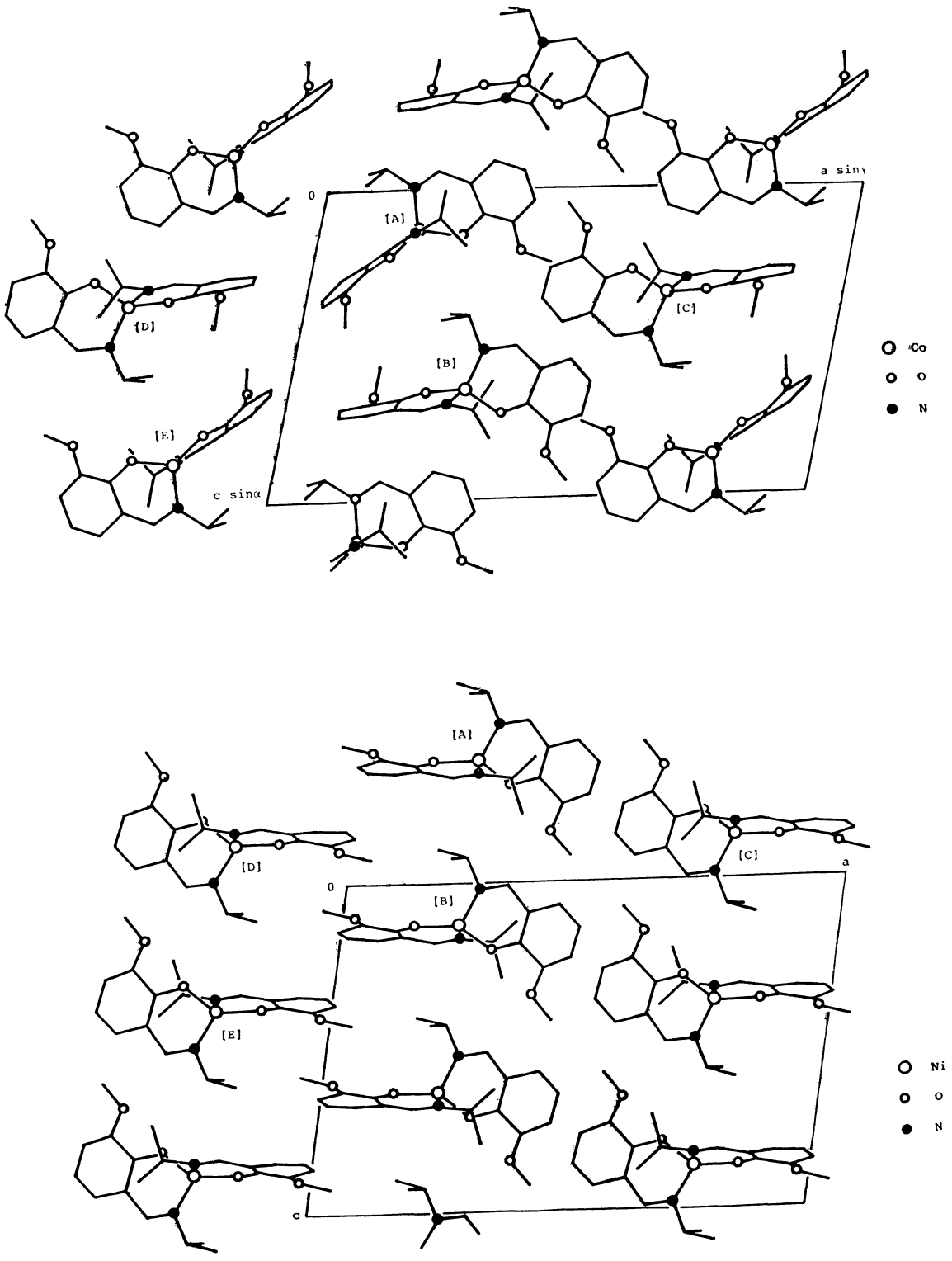

Fig. 6. The crystal structures viewed along the *b* axes; top, Co complex; bottom, Ni complex.

TABLE 6. Co(3-CH_3O-SAL·*i*-C_3H_7)$_2$: BEST PLANES
Planes I and II: each half of the molecule.
Planes III and IV: isopropyl groups.

(a) Equations* $lX+mY+nZ=p$

	l	m	n	p
Molecule A				
I	0.1557	0.9269	−0.3414	−0.5049
II	−0.5632	−0.1421	−0.8141	−3.7144
III	−0.4273	−0.1659	−0.8888	−0.0197
IV	−0.0991	−0.9634	0.2491	−2.5999
Molecule B				
I	−0.2537	0.9588	−0.1282	−3.5352
II	−0.1262	−0.2215	−0.9670	−8.8492
III	0.0620	−0.0763	−0.9952	−5.0049
IV	−0.1378	0.9654	−0.2216	−6.9555

* orthogonal coordinate system in Å unit, X along the a axis, Y in the ab plane

(b) Dihedral angles (°)

	Molecule A			Molecule B		
	II	III	IV	II	III	IV
I	86.6	85.2	6.6	86.8	87.8	8.6
II		9.0	89.4		13.8	89.0
III			88.9			82.4

(c) Displacements from planes (×10^3 Å)

Plane I			Plane II		
Molecule	A	B	Molecule	A	B
C (1)	52	−53	C (21)	84	43
C (2)	13	2	C (22)	44	38
C (3)	−50	52	C (23)	−62	−13
C (4)	−19	18	C (24)	−54	−6
C (5)	9	−57	C (25)	56	11
C (6)	−1	−109	C (26)	112	51
C (7)	22	22	C (27)	−10	−15
C (8)	−56	282	C (28)	−240	−154
N (1)	35	4	N (2)	−8	33
O (1)	−36	18	O (3)	70	9
O (2)	−66	94	O (4)	−177	−113
Co	185	−231	Co	227	122
C (11)*	−45	175	C (31)*	−1064	1035

* Not included in the estimations of the equations.

The only distinct difference in the molecular structures of the present complexes exist in the methoxy groups. In the Ni complex the methoxy group is coplanar with the phenyl plane to which it is attached. In the Co complexes, one methoxy group is coplanar with the pheny plane, but the other sticks out nearly perpendicularly from the phenyl plane. As shown in Figs. 4 and 6, the orientations of the latter methoxy groups are opposite in the two molecules, A and B.

To our knowledge, the methoxyphenyl group is usually planar, because the planar stucture with a larger conjugate system is usually more stable than the non-planar stucture with a smaller conjugate system. The present Co complex gives a unique example of the non-planar methoxyphenyl group. The bond distances and angles are affected seriously by the orientations of the methoxy groups. The mean values of the bond distances and angles in each of the planar and non-planar structures in the Co complex are shown in Fig. 3, while those for the planar structures reported so far[12] are shown in Fig. 5. In the planar structures the repulsion between the methyl group and the peri-hydrogen atom of C(4) makes the O(2)–C(3)–C(4) angle significantly larger than 120°. The inequality in two bond distances of O(2)–CH_3 and O(2)–C(3) is also characteristic of the planar stucture. The latter bond is shorter than usual O–C single bond. In the non-planar structure the O(2)–C(3)–C(4) angle decreases to the normal value, and the inequality in the two C–O bond distances disappears.

Crystal Structure

The crystal structures viewed along the b axes are compared in Fig. 6. As was expected from the similarity in the unit cell dimensions, two crystals are isostructural in a very rough comparison. The orientations of the Co complexes A and B are not so different from those of the Ni complexes A and B which are related by a c glide plane. The packing schemes in the crystals are also similar to each other. Therefore, the intermolecular potential energies due to the van der Waals forces seem to be almost equal in the two crystals. The difference, however, is singificant, and seems to be in entropy. The crystal of the Ni complex is in a highly ordered state with smaller entropy, while the crystal of the Co complex is in a less ordered state with larger entropy.

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