Preparation and Stereochemistry of the Cobalt(III) Complexes with *N,N'*-Polymethylenedi(salicylideneamine) and Its Related Compounds

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Preparation of two series of the cobalt(III) complexes, Na[Co(CN)$_2$(SB)] and [Co(acac)(SB)], was carried out. CN, acac and SB respectively refer to cyanide anion, acetylacetonate anion and the quadridentate Schiff base anion, *N,N'*-polymethylenedi(salicylideneamine), *N,N'*-polymethylenedi(α-methylsalicylideneamine) or *N,N'*-polymethylenedi(2-hydroxy-1-naphthylmethyleneamine). Efforts to obtain Na[Co(CN)$_2$(SB)] only containing the last Schiff base were unsuccessful. It was concluded from their PMR spectra that, for the dicyano complexes, the structure changes from a *trans*-form to a *cis*-one *via* a distorted *trans*-form, whereas for the acetylacetonato complexes, it changes from a distorted *cis*-*β*-form to an undistorted one with an increase in the length of carbon chain in the bridged polymethylene group of the Schiff bases.

The preparation of the first transition, bivalent metal complexes with salrn as the Schiff base is well-known. Salrn is the abbreviated form of *N,N'*-polymethylenedi(salicylideneamine), $HOC_6H_4CH{=}N(CH_2)_nN{=}CHC_6H_4OH$, which is indicated by salen, saltn and salbn when $n=2$, 3, and 4, respectively. Their structures change from the planar coordination of Schiff base to nonplanar tetrahedral coordination with an increase in the length of carbon chain in the bridged polymethylene group of the Schiff bases from $n=2$ through $n=4$ in Co(II), Ni(II), Cu(II), and Zn(II) complexes.[1-13)]

In the tervalent metal complexes, only the cobalt(III) complex containing the above Schiff base as a ligand, where $n=2$, is known.[1,14,15)] No other complexes containing bases where n is greater than 3 have been prepared.

Since tervalent metal complexes generally prefer a hexacoordinated octahedral structure, the coordination feature of the Schiff base seems to depend on both the potential denticity of the ligand simultaneously coordinated and the length of carbon chain of the polymethylene bridge.

In the series Na[Co(CN)$_2$(salrn)], when $n=2$, the complex is known to take a *trans*-form structure.[16,17)] However, the greater the carbon chain lengthens, the greater the steric strain on the *trans*-form structure.

On the other hand, in the series [Co(acac)(salrn)], when $n=2$, the complex is assumed to take a remarkably distorted *cis*-*β*-form structure, due to the occupancy of adjacent sites by bidentate acetylacetonate.[18-20)] However, as the length of the carbon chain of the polymethylene bridge increases, the above distortion is expected to disappear in contrast to the complexes Na[Co(CN)$_2$(salrn)].

In the present work, the change in the expected steric effect was studied by measuring the PMR spectra of the two series.

In order to confirm the results of PMR spectra of the complexes containing salrn, similar studies were carried out for Na[Co(CN)$_2$(Me-salrn)] and [Co(acac)(Me-salrn)] (Me-salrn is the abbreviated form of *N,N'*-polymethylenedi(α-methylsalicylideneamine) anion, $HOC_6H_4C(CH_3){=}N(CH_2)_nN{=}C(CH_3)C_6H_4OH$, which is indicated by Me-salen, Me-saltn, and Me-salbn when $n=2$, 3, and 4, respectively). Preparation was also made of the cobalt(III) complexes [Co(acac)(Np-salrn)], and their PMR spectra were measured for the sake of stereochemical comparison with the corresponding three types of Schiff base complexes (Np-salrn is the abbreviated form of *N,N'*-polymethylenedi(2-hydroxy-1-naphthylmethyleneamine) anion, $HOC_{10}H_6CH{=}N(CH_2)_nN{=}CHC_{10}H_6OH$, which is indicated by Np-saltn and Np-salbn when $n=3$ and 4, respectively).

Experimental

Preparation. *Co(II) Complexes*: The Schiff bases and the cobalt(II) complexes containing them were prepared by the procedure given by Hariharan and Urbach[4)] and identified by elemental analysis.

Co(III) Complexes. *1)* trans-*Sodium Dicyano*-N,N'-*ethylenedi(salicylideneaminato)cobaltate(III)*, trans-*Na[Co(CN)$_2$(salen)] (I)*: Ten milliliters of aqueous solution containing 0.022 mol of sodium cyanide was added to 100 ml of ethanolic solution containing 0.01 mol of Co(II)-Schiff base complex, [Co(salen)] in suspension, and the resulting solution was stirred for 10 min. On being oxidized by blow of air for 2—10 h, yellowish orange powder was precipitated. Needle crystals were separated out by recrystallization from aqueous solution containing a small amount of sodium cyanide. Yield, about 50%. Found: N, 13.90; C, 53.98; H, 3.85%. Calcd for Na[Co(CN)$_2$(salen)]: N, 14.00; C, 54.01; H, 3.53%.

2) trans-*Sodium Dicyano*-N,N'-*trimethylenedi(salicylideneaminato)cobaltate(III) Monohydrate*, trans-*Na[Co(CN)$_2$(saltn)]·H$_2$O(II)*: The procedure of preparation was similar to that for Complex I, [Co(saltn)] being used as Co(II) Schiff base complex of the starting materials, in place of [Co(salen)]. When the resulting solution was oxidized, concentrated to 15 ml at 20 °C, and then allowed to stand overnight in a refrigerator, brown needle crystals were separated out. Recrystallization was achieved by the same procedure as that used for Complex I. Yield, about 40%. Found: N, 12.88; C, 54.81; H, 4.20%. Calcd for Na[Co(CN)$_2$(saltn)]·H$_2$O: N, 12.96; C, 52.78; H, 4.21%.

3) cis-*β*-*Sodium Dicyano*-N,N'-*tetramethylenedi(salicylideneaminato)cobaltate(III) Trihydrate*, cis-*β*-*Na[Co(CN)$_2$(salbn)]·3H$_2$O (III)*: This complex was prepared by a procedure similar to that employed for Complex II, [Co(salbn)] being used in place of [Co(saltn)]. Brown cubic crystals were obtained. Recrystallization was carried out from ethanol–ether mixture. Yield, about 30%. Found: N, 11.72; C, 50.92; H, 5.34%. Calcd for Na[Co(CN)$_2$(salbn)]·3H$_2$O: N, 11.62; C, 49.83; H, 5.02%.

4) trans-*Sodium Dicyano*-N,N'-*ethylenedi(α-methylsalicylideneaminato)cobaltate(III) Monohydrate,* trans-*Na[Co(CN)$_2$(Me-salen)]·H$_2$O (IV)*: This complex was prepared and recrystallized by a procedure similar to that employed for Complex I, Me-salen being used in place of salen as a Schiff base. Orange crystals were obtained. Yield, 50%. Found: N, 12.40; C, 54.18; H, 4.44%. Calcd for Na[Co$(CN)_2$(Me-salen)]·H_2O: N, 12.56; C, 53.83; H, 4.53%.

5) trans-*Sodium Dicyano*-N,N'-*trimethylenedi(α-methylsalicylideneaminato)cobaltate(III) Dihydrate,* trans-*Na[(CN)$_2$(Me-saltn)]·2H$_2$O (V)*: This complex was also prepared and recrystallized by a procedure similar to that employed for Complex II, Me-saltn being used in place of saltn as a Schiff base. Brown needle crystals were obtained. Yield, about 40%. Found: N, 11.48; C, 54.54; H, 5.38%. Calcd for Na[Co$(CN)_2$(Me-saltn)]·$2H_2O$: N, 11.71; C, 52.72; H, 5.07%.

6) cis-α-*Sodium Dicyano*-N,N'-*tetramethylenedi(α-methylsalicylideneaminato)cobaltate(III) Dihydrate,* cis-α-*Na[Co(CN)$_2$(Me-salbn)]·2H$_2$O (VI)*: This complex was also prepared and recrystallized by a procedure similar to that employed for Complex III, Me-salbn being used in place of salbn as a Schiff base. Yellowish green needle crystals were obtained. Yield, about 20%. Found: N, 11.32; C, 54.97; H, 5.44%. Calcd for Na[Co$(CN)_2$(Me-salbn)]·$2H_2O$: N, 11.38; C, 53.66; H, 5.33%.

Coordination of the cyano group for Complexes I—VI was confirmed from the IR spectra. The charge of these complexes was confirmed by the behavior to an anion exchanger.

7) cis-*β-Acetylacetonato*-N,N'-*ethylenedi(salicylideneaminato)cobalt(III) Quarterhydrate,* cis-*β-[Co(acac)(salen)]·0.25H$_2$O (VII)* This complex was prepared by a modification of the procedure of Fujii *et al.*[17] Ten milliliters of aqueous solution containing 0.006 mol of potassium acetylacetonate was added to 100 ml of methanolic solution suspending 0.005 mol of Co(II)-Schiff base complex, [Co(salen)], and the solution was oxidized by hydrogen peroxide. The resulting solution was refluxed for 1 h and concentrated to *ca.* 20 ml. When the solution was let to stand overnight in a refrigerator, dark green crystals were separated out. They were recrystallized from methanol. Yield, about 70%. Found: N, 6.49; C, 58.60; H, 5.01%. Calcd for [Co(acac)(salen)]·$0.25H_2O$: N, 6.53; C, 58.80; H, 5.06%.

8) cis-*β-Acetylacetonato*-N,N'-*trimethylenedi(salicylideneaminato)cobalt(III) Quarterhydrate,* cis-*β-[Co(acac)(saltn)]·0.25H$_2$O (VIII)*: This complex was prepared and recrystallized by a procedure similar to that employed for Complex VII, saltn being used in place of salen. Dark green crystals were obtained. Yield, about 70%. Found: N, 6.20; C, 59.92; H, 5.44%. Calcd for [Co(acac)(saltn)]·$0.25H_2O$: N, 6.33; C, 59.65; H, 5.36%.

9) cis-*β-Acetylacetonato*-N,N'-*tetramethylenedi(salicylideneaminato)cobalt(III) Hemihydrate,* cis-*β-[Co(acac)(salbn)]·0.5H$_2$O (IX)*: This complex was also prepared and recrystallized by a procedure similar to that employed for Complex VII, salbn being used in place of salen. Bluish green crystals were obtained. Yield, about 60%. Found: N, 5.93; C, 59.75; H, 6.04%. Calcd for [Co(acac)(salbn)]·$0.5H_2O$: N, 6.07; C, 59.86; H, 6.04%.

10) cis-*β-Acetylacetonato*-N,N'-*ethylenedi(α-methylsalicylideneaminato)cobalt(III),* cis-*β-[Co(acac)(Me-salen)] (X)*: This complex was also prepared and recrystallized by a procedure similar to that employed for Complex VII, Me-salen being used in place of salen. Dark green crystals were obtained. Yield, about 70%. Found: N, 6.18; C, 61.03; H, 15.66%. Calcd for [Co(acac)(Me-salen)]: N, 6.18; C, 61.05; H, 15.58%.

11) cis-*β-Acetylacetonato*-N,N'-*trimethylenedi(α-methylsalicylideneaminato)cobalt(III) Monohydrate,* cis-*β-[Co(acac)(Me-saltn)]·H$_2$O (XI)*: This complex was also prepared and recrystallized by a procedure similar to that employed for Complex VII, Me-saltn being used in place of salen. Dark green crystals were separated out. Yield, about 70%. Found: N, 5.78; C, 59.55; H, 5.96%. Calcd for [Co(acac)(Me-saltn)]·H_2O: N, 5.78; C, 59.49; H, 6.05%.

12) cis-*β-Acetylacetonato*-N,N'-*tetramethylenedi(α-methylsalicylideneaminato)cobalt(III),* cis-*β-[Co(acac)(Me-salbn)] (XII)*: This complex was also prepared and recrystallized by a procedure similar to that employed for Complex VII, Me-salbn being used in place of salen. Bluish green crystals were obtained. Yield, about 60%. Found: N, 5.57; C, 62.26; H, 6.17%. Calcd for [Co(acac)(Me-salbn)]: N, 5.83; C, 62.49; H, 6.10%.

13) cis-*β-Acetylacetonato*-N,N'-*trimethylenedi(2-hydroxy-1-naphthylmethyleneaminato)cobalt(III) Hemihydrate,* cis-*β-[Co(acac)(Np-saltn)]·0.5H$_2$O (XIII)*: To 0.01 mol of bis-(acetylacetonato)cobalt(II) dihydrate in 150 ml of chloroform was added 0.01 mol of the Schiff base, Np-saltnH_2, in 20 ml of chloroform. When the solution was refluxed for 1 hr, the color of the solution turned from pink to dark green. The resulting solution was concentrated to *ca.* 20 ml and let to stand overnight in a refrigerator. Dark green columnar crystals were separated out. They were recrystallized from methanol–chloroform mixture. Yield, about 70%. Found: N, 5.12; C, 65.16; H, 5.36%. Calcd for [Co(acac)(Np-saltn)]·$0.5H_2O$; N, 5.12; C, 65.80; H, 5.17%.

14) cis-*β-Acetylacetonato*-N,N'-*tetramethylenedi(2-hydroxy-1-naphthylmethyleneaminato)cobalt(III) Monohydrate,* cis-*β-[Co(acac)(Np-salbn)]·H$_2$O (XIV)*: This complex was prepared and recrystallized by a procedure similar to that employed for Complex XIII, Np-salbn being used in place of Np-saltn. Bluish green columnar crystals were obtained. Yield, about 60%. Found: N, 5.23; C, 64.72; H, 5.47%. Calcd for [Co(acac)(Np-salbn)]·H_2O: N, 4.91; C, 65.25; H, 5.49%.

Coordination of the acetylacetonate group for Complexes VII—XIV was confirmed from the IR spectra; the characteristic absorption band of coordinated acetylacetonate was observed in the vicinity of 1515 cm^{-1}. Preparation of the cobalt(III) complexes with Np-salen was unsuccessful.

Measurement. The PMR spectra of the complexes were measured with a JEOL JNM-MH-60 spectrometer (60 MHz) at 25 °C using D_2O, CD_3OD or $CDCl_3$ as a solvent. TMS or NaTMS was used as an internal reference in all the PMR measurements.

The visible and UV absorption spectra were measured with a 323 Hitachi recording spectrophotometer at room temperature using H_2O or $CHCl_3$ as a solvent.

Results and Discussion

1) Dicyano Complexes, Na[Co(CN)$_2$(SB)]. Three geometrical isomers, *trans*, *cis*-α and *cis*-β-form, are possible for a mixed cobalt(III) complex with a quadridentate ligand and two unidentate ligands. Yamada *et al.*[16] reported that [Co$(CN)_2$(salen)]$^-$ ion has a *trans*-form structure. On the other hand, from a consideration of the molecular model it is presumed that it becomes difficult for [Co$(CN)_2$(salrn)]$^-$ ion to have a *trans*-form with an increase in the length of the bridged polymethylene group owing to increasing distortion. The coordination structure of Na[Co$(CN)_2$(salrn)] and Na[Co$(CN)_2$(Me-salrn)] is thus expected to change from *trans*- to *cis*-form depending on the increase in the

Table 1. PMR spectral data of the dicyano complexes

Complex	Solvent	Peaks of Schiff base (ppm)			
		CH=N or CH_3-C=N	Aromatic ring	=N-CH_2-	-CH_2-
Complex I	D_2O	7.73	6.30—7.30[a]	3.68	
II	D_2O	7.40	6.20—7.20	3.70—3.90[a]	1.87—2.20[a]
III	D_2O	7.67, 8.23	6.50—7.50	3.40—3.77	1.67—2.20
IV	D_2O	2.63	6.50—7.83	3.83	
V	CD_3OD	2.71	6.50—7.50	3.70—3.93	1.85—2.15
VI	CD_3OD	2.51	6.40—7.60	3.80—4.10	1.63—2.00

a) Multiplet peaks.

length of the bridged polymethylene group.[21]

The PMR spectral data of the dicyano complexes, I through VI, are summarized in Table I. The assignment of each signal in their spectra was given on the basis of the corresponding assignment in the complexes[17] which have similar structures to those of dicyano complexes. In Complexes I and IV, one signal of azomethine proton and one signal of azomethyl proton were observed, respectively. In Complexes II and V, patterns similar to those of Complexes I and IV, respectively, were observed. By referring the patterns to those determined to be *trans*-form,[17] the structures of Complexes I, II, IV, and V can all be assigned to a *trans*-form.

However, the azomethine signal of Complex II is found to shift to higher magnetic field as compared with that of Complex I. From a consideration of the molecular model, such a shift seems to be attributed to the fact that the distortion owing to the steric strain of trimethylene group results in a decreased donation power of the ligand to cobalt(III) ion and, consequently, in an increased electron density of ligand in itself and in an increased shielding effect against the methine proton.

On the other hand, in Complex III, since two signals of azomethine proton were observed, the structure can be assigned to a *cis*-β-form.[17]

Similar features found in Complexes I and II could not be distinctly observed in IV and V. The PMR spectrum of Complex IV was measured in D_2O owing to the small solubility in CD_3OD and, inversely, that of Complex V was measured in CD_3OD owing to the small solubility in D_2O. However, in Complex VI, one signal of azomethyl proton was observed in a higher magnetic field region than in Complex V. The structure of Complex VI seems to be forced into a *cis*-form by the steric strain of the bridged tetramethylene group. From the observation of only one signal concerning azomethyl proton, its structure could be assigned to a *cis*-α-form.

2) *Acetylacetonato Complexes, [Co(acac)(SB)].* For these complexes two geometrical isomers, *cis*-α and *cis*-β-form, are possible since acetylacetonate anion acts as a bidentate ligand. Calligaris *et al.*[18] found by X-ray analysis that the structure of Complex VII takes a distorted *cis*-β-form. This structure is in approximate agreement with that expected by Fujii *et al.*[17] The distortion seems to be due to the shorter length of the bridged ethylene group on salen. It is expected that the greater the length of the bridged group (from salen to salbn), the more weakened the distortion in *cis*-β-form.

The PMR spectral data of the acetylacetonato complexes in chloroform are summarized in Table 2. The assignment of each signal in their spectra was made by referring to that of Complex VII.[17,22] In Complexes VII, VIII, and IX, both the signals of azomethine proton of the coordinated Schiff base and methyl proton of coordinated acetylacetonate were split into two peaks, their four signals being in a relative intensity of 1 : 1 : 3 : 3. In Complexes X, XI, and XII, and Complexes XIII and XIV, similar splittings were observed in relative intensities of 3 : 3 : 3 : 3 and 1 : 1 : 3 : 3, respectively. These patterns correspond to those of *cis*-β-form and, therefore, the structures of all the acetylacetonato complexes can be assigned to a *cis*-β-form.

Some characteristics were found in the spectra: in each of the salrn complexes VII, VIII, and IX, and Me-salrn complexes X, XI, and XII, the apparent separation of two split methyl signals of coordinated acetyl-

Table 2. PMR spectral data of the acetylacetonato complexes in $CDCl_3$

Complex	Peaks of Schiff base (ppm)				Peaks of acac (ppm)	
	CH=N or CH_3-C=N	Aromatic ring	=N-CH_2-	-CH_2-	CH=C	CH_3-
Complex VII	7.60, 7.83	6.40—7.45[a]	3.87—4.13[a]		5.43	1.81, 2.00
VIII	7.43, 7.60	6.30—7.35	3.22—3.70	2.10—2.50[a]	5.45	1.92, 2.12
IX	7.44, 7.63	6.35—7.30	3.00—4.00	1.85—2.50	5.35	1.64, 2.05
X	2.61, 2.76	6.45—7.75	3.90—4.30		5.39	1.82, 1.84
XI	2.62, 2.69	6.40—7.45	3.45—4.04	1.95—2.30	5.26	1.40, 1.78
XII	2.64, 2.71	6.20—7.45	3.50—4.00	1.80—2.20	5.21	1.25, 1.67
XIII	7.89, 8.25	7.06—7.80	3.50—4.00	2.00—2.50	5.40	1.83, 1.92
XIV	8.10, 8.22	7.00—7.80	3.30—3.80	1.80—2.50	5.26	1.53, 1.95

a) Multiplet peaks.

acetonate increases with the increase in the length of the bridged group, where one signal is apparently fixed and the other is shifted to a higher magnetic field. Two methine signals of the coordinated Schiff base for Np-salrn complexes XIII and XIV are shifted to a lower magnetic field than that of salrn complexes VIII and IX. The apparent separation of the corresponding split signals also has a tendency to increase in VIII and IX, and also XIII and XIV, with an increase in the length of the bridged group.

The first tendency may be related to the degree of distortion of the coordination structure in these complexes, but the origin is still obscure. The anisotropic effects of phenyl and naphthyl skeleton of the coordinated Schiff bases seem to play a less important role because of the large distance between methyl groups of acetylacetonate and these skeletons.[23] Other effects, such as solvent effect *etc*, might play an effective role. The origin of the second tendency may be related to the greater deshielding effect of the naphthyl skeleton in Complexes XIII and XIV than that of the phenyl skeleton in Complexes VIII and IV.

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References

1) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).
2) W. P. Schafer and R. E. Marsh, *Acta Crystallogr.*, **B 25**, 1675 (1970).
3) H. Weigold and B. O. West, *J. Chem. Soc.*, *A*, **1967**, 1310.
4) M. Hariharan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969).
5) J. Manassen, *ibid.*, **9**, 966 (1970).
6) H. Montgomery and B. Morosin, *Acta Crystallogr.*, **12**, 551 (1961).
7) L. M. Shkol'nikova, E. A. Shugam, and L. G. Makarevich, *Zh. Strukt. Khim.*, **4**, 927 (1963).
8) R. H. Holm, *J. Amer. Chem. Soc.*, **82**, 5632 (1960).
9) W. C. Hoyt and G. W. Everett, Jr., *Inorg. Chem.*, **8**, 2013 (1969).
10) D. Hall and T.N. Waters, *J. Chem. Soc.*, *A*, **1960**, 2644.
11) E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969); S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Nucl. Chem. Lett.*, **4**, 107 (1968); *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).
12) T. P. Cheeseman, D. Hall, and T. N. Waters, *Proc. Chem. Soc.* (London), **1963**, 379.
13) G. E. Batley and D. P. Graddon, *Aust. J. Chem.*, **20**, 885 (1967).
14) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972).
15) M. D. Hobday and T. D. Smith, *ibid.*, **9**, 311 (1972).
16) S. Yamada, H. Nishikawa, and E. Yoshida, *Proc. Japan Acad.*, **40** 211 (1964).
17) Y. Fujii, A. Osawa, Y. Furukawa, F. Ebina, and S. Takahashi, This Bulletin, **45**, 2459 (1972).
18) M. Calligaris, G. Manzini, G. Nardin, and L. Randaccio, *J. Chem. Soc.*, *Dalton*, **1972**, 543.
19) N. A. Bailey, B. M. Higson, and E. D. McKenzie, *ibid.*, **1972**, 503.
20) D. Cummins, B. M. Higson, and E. D. McKenzie, *ibid.*, **1973**, 1359.
21) G. T. Morgen and J. D. Smith, *J. Chem. Soc.*, **127**, 2030 (1925).
22) R. J. Cozens and K. S. Murray, *Aust. J. Chem.*, **25**, 911 (1972).
23) H. M. McConnell, *J. Chem. Phys.*, **29**, 1012 (1958).