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# The Stereochemistry of Tetradentate Schiff Base Complexes of Cobalt(II)[1]

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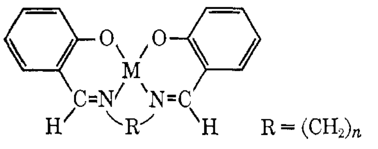
A homologous series of cobalt(II) complexes with N,N′-bis(salicylidene)polymethylenediamine ligands, $HOC_6H_4CH{=}N(CH_2)_nN{=}CHC_6H_4OH$, where $n = 3$–6, has been prepared and characterized. Spectral and magnetic properties indicate that the anhydrous complexes with $n = 4$–6 are pseudo-tetrahedral. The anhydrous trimethylene complex is high spin but does not possess spectral properties similar to the higher members of the series. This is interpreted by assuming a flattened tetrahedral structure for the trimethylene complex, but a weak association leading to a dimeric structure with each cobalt ostensibly five-coordinate may not be ruled out. Mass spectrometric determinations of molecular weights provide evidence for the monomeric nature of the series of complexes.

## Introduction

The factors which determine the stereochemistry of four-coordinate complexes have been elucidated for bis-bidentate-chelates[2] with nickel(II) and cobalt(II). The metal complexes, **1**, containing tetradentate ligands, also offer the possibility of existing in square-planar or tetrahedral forms depending on the number of methylene groups in the central chelate ring. This prospect has been the subject of numerous investigations with both transition and nontransition metal ions.[3-8] The nickel(II) and copper(II) derivatives of **1** exhibit a decrease in ligand field strength as the number of methylene groups is increased from 2 to 4; however the nickel(II) complexes maintain a spin-paired, square-planar geometry even when four bridging carbon atoms are present.[3] This preference for a square-planar structure for Ni(II) is also reported for the corresponding Schiff base complexes derived from pyrrole-2-carboxaldehyde and diamines with two to five methylene groups.[9] For the copper(II) derivatives of **1**, the decrease in ligand field strength, coupled with the small but significant increase in magnetic moments as the bridge length increases, is interpreted as being indicative of an increasing distortion from planarity toward a tetrahedral geometry.[8]



**1**

It is well known that cobalt(II) shows a more pronounced tendency for the formation of tetrahedral complexes than does either nickel(II) or copper(II).[10] For the well-known complex N,N′-bis(salicylidene)-ethylenediaminocobalt(II), a low-spin, square-planar structure has been found.[4,11-13] This structure is no doubt imposed by the steric requirements of the ligand. Increasing the number of methylene carbons between the azomethine groups should relax the structural requirements of the ligand, and the cobalt(II) ion may assume a tetrahedral geometry to relieve the steric interactions in the polymethylene bridge. The cobalt(II) complexes of **1** with seven to ten carbons atoms in the central chelate ring have been prepared and shown by spectral and magnetic properties to have a pseudo-tetrahedral geometry.[4] Molecular weight data could not be obtained and the possibility of polynuclear chelates was not precluded. The corresponding cobalt(II) complexes with less than seven methylene carbons could not be obtained by previous workers.[4,14] In this paper we report the preparation and characterization of the cobalt(II) complexes, **1**, in the region of chelate ring size where an interconversion from square-planar to tetrahedral geometry should occur.

## Experimental Section

**Preparation of the Ligands.**—The ligands were prepared by refluxing 0.05 mol of salicylaldehyde (Eastman) and 0.025 mol of the aliphatic diamine (Aldrich) in 30 ml of methanol for 15 min and cooling the reaction mixture. The Schiff bases separated as yellow needles and were recrystallized twice (methanol); yields 80–90%.

**Preparation of the Cobalt(II) Complexes.**—The general method of preparation was as follows. To a warm solution of 0.01 mol of the Schiff base and a slight molar excess of triethylamine in 200 ml of methanol was added 100 ml of methanol containing 0.01 mol of cobalt chloride hexahydrate. The complexes formed readily and precipitated from these solutions. The solid complexes were filtered, washed with acetone to remove any uncomplexed ligand, and dried *in vacuo*. Owing to their insolubility none of the complexes was successfully recrystallized. To avoid oxidation, the complexes were prepared and handled in a nitrogen

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[2] G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968), and references therein.

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[14] H. Diehl, L. M. Liggett, C. C. Hach, G. C. Harrison, L. Henselmeier, R. W. Schwandt, and J. Mathews, *Iowa State College J. Sci.*, **22**, 110 (1947).

atmosphere. After drying, however, the complexes were all found to be stable toward air and nonhygroscopic over the course of several hours. The following specific results were obtained.

TABLE I
ANALYTICAL DATA FOR THE SCHIFF BASE LIGANDS

| R | % C Calcd | % C Found | % H Calcd | % H Found | % N Calcd | % N Found | Mp, °C[a] |
|---|---|---|---|---|---|---|---|
| $(CH_2)_3$ | 72.33 | 72.40 | 6.43 | 6.51 | 9.93 | 10.00 | 53 |
| $(CH_2)_4$ | 72.46 | 72.93 | 6.76 | 6.66 | 9.38 | 9.54 | 92 |
| $(CH_2)_5$ | 73.50 | 72.74 | 7.14 | 7.10 | 9.03 | 9.06 | 62 |
| $(CH_2)_6$ | 74.08 | 73.62 | 7.46 | 7.28 | 8.64 | 8.38 | 74 |

[a] Uncorrected values.

**N,N′-Bis(salicylidene)trimethylenediaminocobalt(II).**—This compound was previously reported as yellow crystals.[15] It was obtained by our method as a red-brown crystalline dihydrate (after drying *in vacuo* at 100° for 12 hr). *Anal.* Calcd for $C_{17}H_{20}N_2O_4Co$: C, 54.40; H, 5.36; N, 7.44. Found: C, 53.50; H, 4.96; N, 7.47. This compound could be dehydrated without apparent decomposition at 240–250° *in vacuo* for 8 hr. No color change occurred during drying. *Anal.* Calcd for $C_{17}H_{16}N_2O_2Co$: C, 60.19; H, 4.75; N, 8.26. Found: C, 60.58; H, 4.81; N, 8.24.

**N,N′-Bis(salicylidene)tetramethylenediaminocobalt(II).**—This compound was obtained as light green needles and was dried to a red-brown compound *in vacuo* at 184° for 24 hr. *Anal.* Calcd for $C_{18}H_{18}N_2O_2Co$: C, 61.20; H, 5.13; N, 7.93. Found: C, 60.93; H, 5.14; N, 7.78.

**N,N′-Bis(salicylidene)pentamethylenediaminocobalt(II).**—This compound was obtained as light green crystals and was dried to a dark green compound *in vacuo* at 130° for 8 hr. *Anal.* Calcd for $C_{19}H_{20}N_2O_2Co$: C, 62.13; H, 5.49; N, 7.63. Found: C, 61.12; H, 5.56; N, 7.49.

**N,N′-Bis(salicylidene)hexamethylenediaminocobalt(II).**—This compound was obtained as orange-red crystals and was dried *in vacuo* at 130° for 8 hr with no color change. *Anal.* Calcd for $C_{20}H_{22}N_2O_2Co$: C, 63.29; H, 5.82; N, 7.35. Found: C, 62.99; H, 5.84; N, 7.33.

**Bis(N-phenylsalicylaldiminato)cobalt(II).**—This complex prepared by our method (dried *in vacuo* at 130° for 8 hr) was identical with that reported previously.[16]

**Physical Measurements.**—The electronic spectra of the solid complexes were obtained by the reflectance method using a Beckman DK2 recording spectrophotometer with a reflectance attachment and magnesium oxide as the reference material. Magnetic susceptibility measurements were carried out by the Gouy and Faraday methods using $Hg[Co(NCS)_4]$ as a calibrant. Diamagnetic corrections were calculated from tables of Pascal's constants.[17] The magnetic moments determined by the two methods were within ±1% agreement. The mass spectra of the complexes were obtained with the Varian Associates M-66 Cycloidal double-focusing mass spectrometer. The solid compounds were introduced into the ionization chamber using a probe which could be inserted through a vacuum lock system. The peak positions were calibrated using standard substances with known disintegration patterns. Analytical data were obtained by Galbraith Laboratories, Knoxville, Tenn.

## Results and Discussion

Because of the insoluble nature of this series of cobalt(II) complexes, it was not possible to recrystallize the compounds following their preparation. Pure preformed ligands were therefore employed to ensure that the solid complexes which initially formed were of reasonable purity. The analytical data confirm that pure complexes were obtained. The success of this method demonstrates its apparent superiority to the preparation of the complexes by the reaction of diaquobis(salicylaldehydato)cobalt(II) with an appropriate diamine. The insolubility of the cobalt(II) complexes in nondonor solvents also precluded a determination of the coordination geometry in solution. The geometry of these complexes in the solid state was determined by magnetic and spectral measurements.

**Magnetic Properties.**—The observed values of $\mu_{eff}$ for cobalt(II) complexes are generally diagnostic of the coordination geometry about the metal ion. Thus low-spin square-planar cobalt(II) complexes may be readily identified by values for $\mu_{eff}$ in the range 2.1–2.9 BM arising from one unpaired electron plus an apparently large orbital contribution.[18] Tetrahedral and high-spin octahedral cobalt(II) complexes each possess three unpaired electrons but may be distinguished by the magnitude of the deviation of $\mu_{eff}$ from the spin-only value. The magnetic moments of tetrahedral cobalt(II) complexes with an orbitally nondegenerate ground term are increased above the spin-only value *via* contribution from higher orbitally degenerate terms and occur in the range 4.2–4.7 BM.[18] Octahedral cobalt(II), however, maintains a large contribution due to the $^4T_{1g}$ ground term and exhibits $\mu_{eff}$ in the range 4.8–5.6 BM.[18] Fewer data are available for high-spin five-coordinate cobalt(II) complexes; however, the range of values for $\mu_{eff}$ has been given as 4.5–4.8 BM.[19]

The observed values of $\mu_{eff}$ for the series of tetradentate cobalt(II) complexes are given in Table II. The values of $\mu_{eff}$ for the anhydrous complexes immediately eliminate a low-spin square-planar or a high-spin octahedral formulation (achieved through intermolecular bridging) for the complexes. These magnetic moments are in agreement with those expected for tetrahedral cobalt(II); however, a five-coordinate dimeric structure for these complexes cannot be ruled out on the basis of magnetic data alone. Further elucidation of the stereochemistry of these complexes must be made in conjunction with the spectral data (*vide infra*).

TABLE II
ROOM-TEMPERATURE MAGNETIC MOMENTS OF THE TETRADENTATE COBALT(II) COMPLEXES

| R | $10^6\chi_g$, cgsu | $\mu_{eff}$, BM |
|---|---|---|
| $(CH_2)_3 \cdot 2H_2O$[a] | 33.11 | 5.52 |
| $(CH_2)_3$ | 25.00 | 4.56 |
| $(CH_2)_4$ | 21.86 | 4.36 |
| $(CH_2)_5$ | 21.34 | 4.41 |
| $(CH_2)_6$ | 19.92 | 4.33 |

[a] Trimethylene dihydrate complex.

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(15) R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).

(16) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *ibid.*, **84**, 3246 (1962).

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The value of $\mu_{eff}$ for diaquo-N,N'-bis(salicylidene)-trimethylenediaminocobalt(II), although higher than is commonly observed, clearly indicates a pseudo-octahedral geometry for this complex. Values of $\mu_{eff}$ in this range are not unknown for six-coordinate cobalt(II) complexes.[18,20] The assignment of pseudo-octahedral structure to this complex is supported by its electronic spectrum (*vide infra*). The drastic conditions required to dehydrate the complex also favor a structure containing coordinated water molecules.

**Spectral Properties.**—The reflectance spectra of the cobalt(II) complexes are presented in Figures 1 and 2. For the purpose of establishing the stereochemistry of the complexes, the most useful method is to compare these spectra with the spectra of complexes containing similar ligands, for which structures are known. The complex bis(N-phenylsalicylaldiminato)cobalt(II) has been shown by spectral[16] and crystallographic[21] evidence to have a pseudo-tetrahedral geometry. The electronic spectrum[16] (Figure 1) of this complex exhibits absorption bands at 7600, 10,700, 16,700 (sh), and 19,230 cm$^{-1}$ in the near-infrared and visible regions. These band positions are in very good agreement with those obtained for the anhydrous tetradentate cobalt(II) complexes with four to six bridging methylene groups (Figure 1). The spectra of these three tetradentate complexes are also similar to several other bis-bidentate, pseudo-tetrahedral cobalt(II) complexes.[16,22-25] In addition, all of the complexes chosen for spectral comparison possessed magnetic moments in the same range as those obtained for the anhydrous tetradentate complexes. On the basis of these similarities of magnetic and spectral properties with compounds of known structure, it is concluded that when four to six bridging methylene groups are present, sufficient flexibility is introduced into the tetradentate ligands to allow them to adopt a pseudo-tetrahedral geometry about cobalt(II).

A transition assignment may be made for these pseudo-tetrahedral complexes. The transitions at 8000 and 10,000 cm$^{-1}$ are best assigned as low-symmetry components of the second tetrahedral d$^7$ transition, $^4A_2 \rightarrow {}^4T_1(F)$. Bands in the region 17,000-19,000 cm$^{-1}$ may be attributed to the $^4A_2 \rightarrow {}^4T_1(P)$ tetrahedral transition. From their positions and intensities, absorption bands occurring at greater than 20,000 cm$^{-1}$ have been previously assigned to charge-transfer and internal ligand transitions.[16]

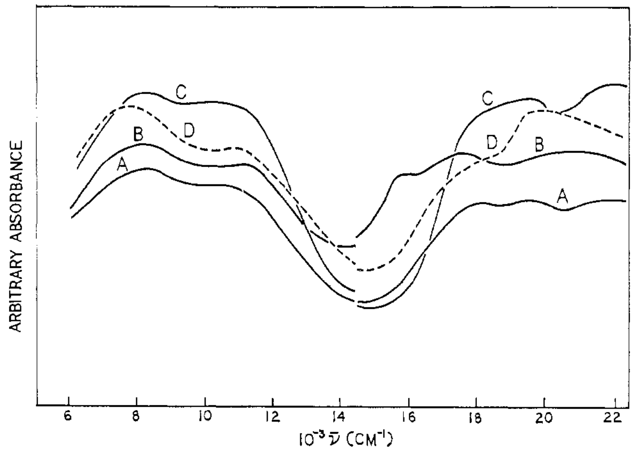

Figure 1.—Reflectance spectra of N,N'-bis(salicylidene)polymethylenediaminocobalt(II) complexes: A, tetramethylene; B, pentamethylene; C, hexamethylene derivatives. D, reflectance spectrum of bis(N-phenyl)salicylaldiminatocobalt(II).

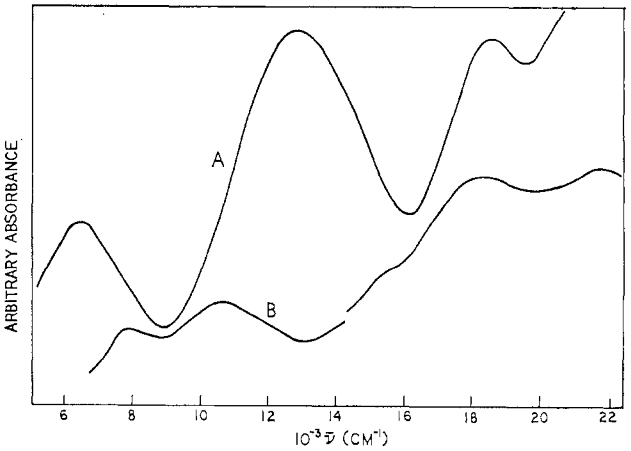

Figure 2.—Reflectance spectra of the anhydrous trimethylene derivative (A) and the trimethylene dihydrate derivative (B) of the cobalt(II) complexes.

The ligand field spectrum of the anhydrous trimethylene complex (Figure 2) does not agree either in band position or in general appearance with the spectra of known pseudo-tetrahedral bis(salicylaldiminato)cobalt(II) complexes. In contrast to the higher homologs, the trimethylene ligand apparently does not have sufficient flexibility to allow the donor atoms to occupy essentially tetrahedral coordination positions. The inability of the trimethylene ligand to form pseudo-tetrahedral complexes has previously been concluded from the fact that beryllium(II), which has a pronounced tendency to form tetrahedral complexes, does not form a 1:1 complex with this ligand but instead forms a 2:1 complex with each ligand functioning as a bidentate chelate.[6]

On the basis of the data available in this study it is not possible to determine unambiguously the stereochemistry of the anhydrous trimethylene derivative. In view of the high-spin nature of the complex and the degree of flexibility in the ligand as indicated by molecular models, the most likely structure for this complex is one in which the donor atoms form a highly flattened tetrahedron. A greatly distorted structure would ac-

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(22) H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962).

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(24) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 2442 (1966).

(25) L. Sacconi and P. L. Orioli, *Ric. Sci. Rend. Sez.*, **A2** (6), 645 (1962).

count for the anomalous spectrum observed for this compound. Although the mass spectral data indicate this complex is monomeric, a dimeric structure, similar to those observed previously,[26] may not be eliminated. The weak intermolecular associations which would be sufficient to produce pentacoordinate cobalt(II) might not persist under the conditions required to obtain the mass spectral data.

A third possible structure for the anhydrous trimethylene complex, *i.e.*, a high-spin, square-planar formulation, is less likely than the structures considered above. The possibility of achieving a high-spin, square-planar cobalt(II) complex has been discussed[27] and such complexes have been reported.[28] Indeed the apparent weakening of the ligand field strength upon going from N,N′-bis(salicylidene)ethylenediamine to the trimethylenediamine derivative favors the high-spin structure. However, the increased flexibility introduced into the ligand with the addtional methylene group would allow the donor atoms to move out of square-planar coordination positions when no strong preference for this geometry is imposed by the metal ion.

In contrast to the anhydrous trimethylene derivative the spectrum of the dihydrate of this complex (Figure 2) is in good agreement with the pseudo-octahedral formulation based on the magnetic data. The spectrum of the dihydrate compares well to the spectra of the bis-pyridine adducts of bis(N-alkyl-3-methoxysalicylaldiminato)cobalt(II) complexes[28] and to the spectra of the six-coordinate cobalt(II) complexes formed with tridentate Schiff base ligands.[29] In this complex the tetradentate ligand probably occupies an approximately square-planar arrangement about the metal ion with two water molecules coordinated in axial positions. Assuming an average in-plane ligand field, the spectrum may be assigned to a tetragonal model. The bands at 8065 and 10,750 cm$^{-1}$ may be assigned to the low-symmetry components of the octahedral $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition. The large splitting of the tetragonal components is reasonable considering the large difference in the ligand field strength between the in-plane and axial ligands. Such a splitting has been predicted by a consideration of the influences of noncubic crystal fields on the metal ion.[30] The remaining bands at 15,300 and 18,520 cm$^{-1}$ are too close in energy to the intense charge-transfer bands to assign them with any certainty to the other octahedral transitions.

**Mass Spectra.**—An important aspect of this problem was to rule out the possibility that the complexes examined in this study possessed polynuclear structures. With increasing length of the polymethylene chain there would be an increased tendency for the potentially tetradentate ligand to bind two metal ions, each in a bidentate fashion. This may result in a binuclear complex similar to those reported previously[31] or in the polymeric structure 2. Since the insolubility of the complexes precluded molecular weight determination in solution, mass spectroscopy was employed to determine the molecular weights of the solid complexes. The mass spectral results together with the required instrumental conditions are given in Table III. For all of the anhydrous chelates, parent ion peaks were obtained which agreed exactly with the molecular weights for the monomeric units. No higher mass peaks were obtained. Caution was exercised to utilize minimum conditions necessary to observe the parent ion peaks for these complexes. The probe temperatures employed were all below the observed decomposition temperatures for the complexes. No fragmentation of the complexes occurred under the experimental conditions employed. For the trimethylene dihydrate compound, however, the water molecules were apparently dissociated from the complex under the conditions required to obtain a signal.

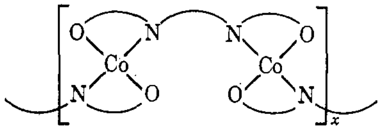

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TABLE III
MASS SPECTRAL DATA FOR THE COMPLEXES[a]

| R | Electron energy, eV | Probe temp, °C | Obsd parent ion peaks, amu |
|---|---|---|---|
| $(CH_2)_3$ | 70 | 240 | 339, 340, 341, 342 |
| $(CH_2)_3 \cdot 2H_2O$ | 70 | 200 | 339, 340, 341, 342 |
| $(CH_2)_4$ | 70 | 160 | 353, 354, 355, 356 |
| $(CH_2)_5$ | 68 | 170 | 367, 368, 369, 370 |
| $(CH_2)_6$ | 71 | 130 | 381, 382, 383, 384 |

[a] Electron current was approximately 40 μA.

## Conclusions

Increasing the length of the methylene bridging group in N,N′-bis(salicylidene)polymethylenediamine ligands leads to the formation of pseudo-tetrahedral complexes with cobalt(II). This is in contrast to the nickel(II) series which maintains a square-planar structure in spite of increasing bridge length. The trimethylene derivative with cobalt(II) cannot adopt a pseudo-tetrahedral structure similar to the higher homologs owing to the restricted nature of this ligand. Further studies are in progress with soluble derivatives of these complexes to determine their preferred stereochemistries in solution.

**Acknowledgment**—The authors wish to thank Mr. W. S. Kehs for his preparation of N,N′-bis(salicylidene)-hexamethylenediaminocobalt(II).

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