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Trinuclear Complexes of Dimethylsilane and Cobalt Schiff-Base Complexes

N. S. BIRADAR, G. V. KARAJAGI, T. M. AMINABHAVI

Department of Chemistry, Karnatak University, Dharwad, India 580003

and W. E. RUDZINSKI*

Department of Chemistry, Southwest Texas State University, San Marcos, Tex. 78666, U.S.A.

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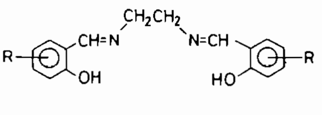
A few trinuclear complexes of cobalt and silicon were synthesized and characterized by elemental analyses, conductivity measurements, magnetic and spectral data. The complexes were shown to have a 1:2 (cobalt–Schiff base:dimethyldichlorosilane) stoichiometry. The complexes were nonelectrolytes in solution, and the stereochemistry around the cobalt changed from square planar to octahedral after the reaction between dimethyldichlorosilane and the Schiff-base cobalt complex.

Introduction

The literature describing the physiological role of silicon in the body has recently been reviewed [1]. Due to the potential applications of silicon compounds in biomedicine, we have been interested in the synthesis and characterization of Schiff-base chelates which react with silicon(IV) [2]. As a continuation of previous work, trinuclear complexes of cobalt Schiff-base and dimethyldichlorosilane have been synthesized. The complexes have been characterized using elemental analyses, conductance measurements, magnetic measurements, uv and infrared spectral measurements.

Experimental

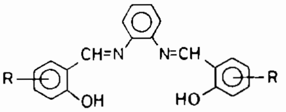
All the chemicals used in this work were of reagent grade. N,N′-bis(salicylidene)ethylenediamine (R-salen) ligands were prepared by heating (15 minutes) an ethanolic solution of the substituted salicylaldehyde (0.1 mol) with ethylenediamine (0.05 mol). N,N′-bis(salicylidene)*o*-phenylenediamine (R-salph) ligands were prepared by heating an ethanolic solution of the substituted salicylaldehyde (0.1 mol) with a phenylenediamine (0.05 mol). The following Schiff-base ligands were prepared:



Ligand	R
A	H
B	4-CH₃
C	4-Cl

Name

A N,N′-bis(salicylidene)ethylenediamine (salen)
B N,N′-bis(4-methylsalicylidene)ethylenediamine (4-CH_3 salen)
C N,N′-bis(4-chlorosalicylidene)ethylenediamine (4-Cl salen)



Ligand	R
D	H
E	4-CH₃
F	4-Cl

Name

D N,N′-bis(salicylidene)*o*-phenylenediamine (salph)
E N,N′-bis(4-methylsalicylidene)*o*-phenylenediamine (4-CH_3 salph)
F N,N′-bis(4-chlorosalicylidene)*o*-phenylenediamine (4-Cl salph)

The cobalt complexes were prepared in a manner similar to that published by Bailes and Calvin [3]. Cobaltous chloride (0.1 mol) was heated for 15 minutes and then added to the respective Schiff-base (A–F). A brown precipitate was formed corresponding to either Co(R-salen)·O or Co(R-salph)·O. The

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*Author to whom correspondence should be addressed.

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product was then filtered, purified and dried over calcium chloride.

The trinuclear complexes were prepared by mixing 0.01 mol of the cobalt Schiff-base with 0.02 mol of dimethyldichlorosilane in chloroform with constant stirring. The brightly-colored complexes formed were then filtered, washed with an excess of chloroform and dried *in vacuo* over P_2O_5. Table I correlates each Schiff-base ligand (A–F) with its corresponding trinuclear complex (I–VI).

Elemental analyses were carried out by a procedure described elsewhere [4]. Cobalt was determined as its pyridine thiocyanate salt. Chlorine was determined as the silver chloride precipitate, while the method of Kjeldahl was used to determine the nitrogen content of the complexes. Carbon and hydrogen were determined using standard analytical techniques.

Conductivities were measured in dimethylformamide (DMF) using an Elico-CM-82 conductivity bridge with a cell constant of 0.829 cm^{-1}. All conductivity measurements were performed at room temperature using 10^{-3} M solutions of complex.

Effective magnetic moments (μ_{eff}) were measured using a Gouy balance at room temperature [5]. All measured susceptibilities were corrected for the diamagnetic contribution of each atom.

The infrared (IR) spectra were obtained from 4000–400 cm^{-1} using a Carl-Zeiss UR-10 infrared spectrometer. Samples were prepared as KBr pellets. Electronic spectra were obtained on a Perkin Elmer 492-5000 spectrophotometer in the region 200–850 nm using 1 cm quartz cells.

TABLE I. Analytical and Physical Data for the Trinuclear Complexes.[a]

Ligand	Number	Complex	% Co	% N	% Cl	% C	% H	Molar Conductivity ohm^{-1} cm^2 mol^{-1}	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ cm^{-1}	μ_{eff} B.M.
A	I	$CoC_{16}H_{14}N_2O_2 \cdot O \cdot [C_2H_6SiCl_2]_2$	9.91 (9.84)	4.70 (4.67)	24.00 (23.70)	40.10 (40.06)	4.31 (4.34)	23.62	21,000	5.27
B	II	$CoC_{18}H_{18}N_2O_2 \cdot O \cdot (C_2H_6SiCl_2]_2$	9.53 (9.40)	4.37 (4.46)	22.70 (22.64)	42.15 (42.10)	5.00 (4.78)	31.71	20,400	5.32
C	III	$CoC_{16}H_{12}N_2O_2Cl_2 \cdot O \cdot [C_2H_6SiCl_2]_2$	9.01 (8.83)	4.23 (4.19)	33.94 (31.85)	39.61 (39.52)	3.56 (3.59)	46.23	20,800	5.40
D	IV	$CoC_{20}H_{14}N_2O_2 \cdot O \cdot [C_2H_6SiCl_2]_2$	9.23 (9.11)	4.30 (4.32)	21.98 (21.94)	44.56 (44.51)	4.09 (4.01)	25.03	20,500	5.37
E	V	$CoC_{22}H_{18}N_2O_2 \cdot O \cdot [C_2H_6SiCl_2]_2$	8.90 (8.74)	4.08 (4.14)	21.14 (21.03)	44.23 (44.22)	4.52 (4.44)	17.86	20,000	5.29
F	VI	$CoC_{20}H_{12}N_2O_2Cl_2 \cdot O \cdot [C_2H_6SiCl_2]_2$	8.31 (8.24)	4.12 (3.91)	29.80 (29.74)	40.36 (40.22)	3.37 (3.35)	13.18	20,400	5.23

[a] Values in parenthesis are theoretical.

Results and Discussion

Analytical Data

All the complexes (I–VI) were colored, amorphous and insoluble in common organic solvents. The complexes are soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The elemental analyses (see Table I) confirm 1:2 (Cobalt Schiff-base:dichlorosilane) stoichiometry. The molar conductivities are in the range 13–46 ohm^{-1} cm^2 mol^{-1} indicating nonelectrolyte behavior in DMF.

Magnetic Properties

The magnetic moments of all the Schiff-base complexes are in the range of 2.2 to 2.6 B.M., a value that is very characteristic for low-spin planar cobalt(II) complexes [6]. The Co(R-salen) complexes are practically diamagnetic at full oxygenation, suggesting spin quenching via a $Co-O_2-Co$ interaction [7]. In the trinuclear complexes I–VI, the magnetic moments are found to be in the range 5.1–5.4 B.M.

The results suggest that the reaction of dimethyldichlorosilane with [Co(R-salen)•O] and [Co(R-salph)•O] involves a stereochemical transformation around cobalt from square-planar to octahedral geometry.

Electronic Spectra

The electronic spectral data for the trinuclear complexes I–VI are listed in the Table. The spectra of the complexes exhibit a wide band in the range 500–475 nm^{-1} (20,000–21,000 cm^{-1}). This band has been observed in the spectra of octahedral cobalt(II) complexes [8, 9]. In general, two absorption bands are observed for octahedral complexes. One band is located in the range 1240–1000 nm (8,000–10,000 cm^{-1}) and the second band in the range 525–450 nm (19,000–22,000 cm^{-1}). The first band is assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$ transition and the second is assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition. A third transition $^4T_{1g} \rightarrow {}^4A_{2g}$, is not normally observed [10]. On the basis of the bands observed at 475–500 nm, and corroborating the magnetic measurements, the trinuclear complexes I–VI are formulated to have octahedral geometry around the cobalt.

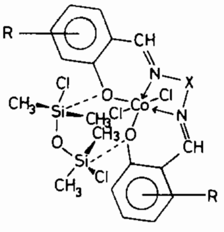
Infrared Spectra

Important IR frequencies and their assignments are available upon request from Dr. T. M. Aminabhavi.

A band observed around 1600 cm^{-1} in the cobalt complexes is attributed to ν(C=N) and this band shifts to around 1630 cm^{-1} after the cobalt complex reacts with dimethyldichlorosilane. The phenolic ν(C–O) also shifts to a higher frequency (1350 cm^{-1}). The increases in frequency suggest that an adduct may have formed between the cobalt complexes and the dimethyldichlorosilanes [11]. A prominent band at 850 cm^{-1} in the trinuclear complexes I–VI is attributed to ν(Si–O) [12]. In conformity with previous observations [13, 14] an intense band around 1030 cm^{-1} is assigned to ν(Si–O–Si). A band at 630 cm^{-1} and a second around 600–570 cm^{-1} are tentatively assigned to ν(Si–C) and ν(Si–Cl) respectively [15]. The ν(Co–N) and ν(Co–O) stretching vibrations around 540 cm^{-1} and 460 cm^{-1} respectively remain unchanged in both the cobalt and trinuclear complexes.

Conclusions

A few trinuclear complexes of cobalt Schiff-base complexes and dimethyldichlorosilane have been synthesized and characterized using elemental analyses, conductivity and magnetic measurements, and electronic and infrared spectral data, The data suggest that the complexes have a 1:2 (cobalt Schiff-base:dimethyldichlorosilane) stoichiometry. The magnetic measurements and electronic spectral data suggest a stereochemical tranformation from square planar to octahedral around the cobalt atom. Based upon the preceding data, the following structure is proposed for the trinuclear complex:



R = H, 4-CH_3, 4-Cl
X = $-C_2H_4-$, $-C_6H_4-$

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