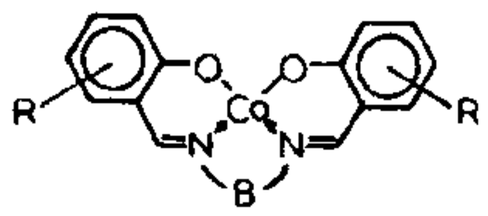
SHORT COMMUNICATIONS

BINUCLEAR ADDUCTS OF SILICON(IV) CHLORIDE WITH TETRADENTATE SCHIFF BASE COBALT(II) COMPLEXES

T. M. AMINABHAVI, N. S. BIRADAR and V. L. RODDABASANAGOUDAR
Department of Chemistry, Karnatak University, Dharwad 580 003, India.



B \ R	H	5–CH_3
$-(CH_2)_2-$	A	B
$-(CH_2)_3-$	C	D
	E	F

DUE to the renewed interest[1-3] in the syntheses of bimetallic complexes of silicon(IV) chlorides with transition metals we report here the syntheses of square planear cobalt(II) complexes with silicon tetrachloride. These were characterized by elemental analysis, magnetic measurements, electronic and infrared spectral data.

All chemicals used here were of reagent grade. The tetradentate schiff bases (A-F) formed from salicylaldehyde and diamines and their cobalt(II) complexes were prepared by known methods[1]. The corresponding bimetallic adducts were prepared by mixing cobalt(II) schiff base complex and silicon(IV) chloride in dry chloroform in the same molar structure ratio. The reaction mixture was left at room temperature for several hours with occasional shaking. The bright coloured microcrystalline solid was filtered and washed with dry chloroform and dried in *vacuo* over P_2O_5. These adducts are soluble in dipolar aprotic solvents. The analytical data (table 1) suggest that these adducts have a 1:1 stoichiometry. The structural assignments of the compounds are based on IR spectra recorded in KBr matrix on an infracord spectrophotometer, (Carl Zeiss UR-10), electronic spectra recorded on a spectrophotometer (Perkin Elmer 492–5000) in the region 200–850 nm and magnetic moments measured on a Guoy balance at room temperature.

The IR spectra of monometallic and bimetallic compounds were compared. The characteristic frequencies of bimetallic adducts are: ν(Si–Cl)[4-6] in the region 635–655 cm^{-1} and ν(Co-Cl)[7] in the region 280-320 cm^{-1}. The electronic spectra of A to F in chloroform show a band at 8,550 cm^{-1} which is characteristic of the square planar environment around cobalt(II)[8]. In the binuclear adducts, the only d-d transition observed in the region 15,300-15,750 cm^{-1} corresponds to $^4A_2 \rightarrow {}^4T_1(P)$ transition(ν_3). The magnetic moments of compounds A to F are in the range of 2.25 to 2.55 B.M. indicating a square planar configuration[9-10]. However, in the adducts these values were found to increase to a range of 4.05 to 4.5 B.M. suggesting an

Table 1 *Physical and analytical data of binuclear adducts*

Mono-metallic compound	Molecular formula of adduct	Found (calc) %				Electronic spectrum ν cm^{-1}	Magnetic moment μ_{eff} B.M.
		Co	Si	N	Cl		
A	$C_{16}H_{14}O_2N_2Cl_4CoSi$	11.86 (11.92)	5.63 (5.66)	5.63 (5 66)	28.30 (28.69)	15,600	4.22
B	$C_{18}H_{18}O_2N_2Cl_4CoSi$	11.13 (11.28)	5.29 (5.35)	5.30 (5.35)	27.02 (27.15)	15,600	4.50
C	$C_{17}H_{16}O_2N_2Cl_4CoSi$	11.43 (11.59)	5.41 (5.50)	5.37 (5.50)	27.86 (27.90)	15,500	4.39
D	$C_{19}H_{20}O_2N_2Cl_4CoSi$	10.67 (10.99)	5.07 (5.21)	5.06 (5.21)	26.69 (26.44)	15,750	4.33
E	$C_{20}H_{14}O_2N_2Cl_4CoSi$	10.92 (10.83)	5.18 (5.14)	5.36 (5.14)	26.12 (26.06)	15,500	4.06
F	$C_{22}H_{18}O_2N_2Cl_4CoSi$	10.63 (10.30)	4.93 (4.89)	4.73 (4.89)	24.60 (24.78)	15,300	4.04

octahedral geometry for binuclear compounds[11,12].

In conclusion it can be stated that the two chlorine atoms of $SiCl_4$ moiety are coordinated to cobalt(II) schiff base moiety in the adduct.

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^{13}C NMR EVIDENCE FOR THE STRUCTURE OF THEVEFOLIC ACIDS

A. G. RAMACHANDRAN NAIR,
R. GUNASEGARAN* and
K. V. RAMANATHAN†

Department of Chemistry, Jawaharlal Institute, Pondicherry 605 006, India.
† Sophisticated Instruments Facility, Indian Institute of Science, Bangalore 560 012, India.
** Present address: Department of Chemistry, Bharathidasan College for Women, Pondicherry 605 001, India.*

Two phenyl lactic acid derivatives named Thevefolic acids A and B were isolated from the more polar fraction of ethanolic extract of fresh flowers of *Thevetia neriifolia*[1]. They were characterized as (+)-methyl-β-(2-hydroxy-4-carboxy phenyl) lactate and (+)-β-(2-hydroxy-4-carboxy phenyl) lactic acid by chemical and spectral methods. Also, the stereochemistry of these compounds was determined subsequently and assigned[2] the R-configuration. Chopin[3] however suggested that though the 1,2,4-substitution of benzene ring in the molecule was beyond doubt, the precise placement of OH and COOH groups in benzene based on the comparison of ^{13}C resonances was not beyond doubt. We have therefore re-examined the structure ot these compounds by analysing the ^{13}c NMR spectrum from different angles and report our confirmation of the earlier structural assignment.

The ^{13}C resonances of aromatic carbons were computed by using the resonances of aromatic carbons of β-phenyl lactic acid and the substitution effect[4] on carbons on introducing 2-OH and 4-COOH as well as 2-COOH and 4-OH to β-phenyl lactic acid and comparing the agreement with observed values. The structure with 2-OH and 4-COOH was in good agreement (Computed: 116.63 *d*, 122.03 *d*, 129.59 *s*, 130.38 *s*, 130.66 *d*, and 156.16 *s*; Observed 115.60 *d*, 120.30 *d*, 129.50 *s*, 130.40 *s*, 131.70 *d* and 155.60 *s*).

The proton coupled ^{13}C spectrum of the compound was recorded with NOE enhancement and the pattern of the coupled carbonyl carbon analysed and compared with the same expected for 2-COOH (4-OH) with two bond coupling with one proton (COO*H* proton) and three bond coupling with another (3-*H*), and 4-COOH (2-OH) with the same two bond coupling but three bond coupling with two protons (3-and 5-*H*). The pattern was in agreement for 4-COOH. The pattern of coupled carbon carrying-OH was so complex that a distinction between 2-OH and 4-OH could not be made to further confirm 2-OH (4-COOH) structure.

A consideration of the linear nature of these molecules and their preferential motion in solution (rotation around the linear axis) will result in observing[5] significant differences in the relaxation time of 2-carbonyl carbon and lactic acid carbonyl carbon while there may not be much difference between 4-carbonyl carbon and lactic acid carbon. The relaxation time (T_1) measured (inversion recovery method) for the two carbonyl carbons (using two τ values, 0.2 sec and 2.0 sec) was found to be the same pointing to 4-COOH structure for the compound.