

Mixed ligand complexes of cobalt(II and III)—Molecular structure of *bis*-(4-acetophenylsalicylaldiminato)acetylacetonato cobalt(III)

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Received 28 June 1999; revised 27 January 2000

The bidentate Schiff bases, HL' (= N-4-acetophenylsalicylal-dimine), H'' (= N-3-acetophenylsalicylal-dimine) and HL''' (= N-4-acetophenyl-5-bromosalicylal-dimine) do not form complexes with simple cobalt(II)salts, e.g., Co(CH₃COO)₂·4H₂O and CoCl₂·6H₂O but undergo facile reactions with Co(acac)₂·2H₂O (acac=monoanion of acetylacetonone). Mixed ligand complexes of both cobalt(III), [Co(L)₂(acac)] and cobalt(II), [Co(L)(acac)] (L=L', L'', L''') have been isolated and characterised by elemental analyses and magnetic susceptibility measurements, electronic, IR and mass spectral studies and by single crystal X-ray crystallographic structure analysis. The cobalt atom is octahedrally coordinated in which four ligand oxygen atoms define an equatorial plane; the two nitrogen atoms of the L' ligands are in *trans*-axial positions.

Mixed Schiff base ligands viz., mono-, homo- and heteronuclear complexes of transition metals are known to find application for understanding many reactions in living processes¹ and many such complexes have been studied as model complexes²⁻⁵. In search of new Schiff base ligands for stabilising complexes of unusual coordination numbers, the Schiff bases HL (L = L', L'', L'''), which have not been reported so far, were not found to undergo any complexation reaction with hydrated cobalt(II) acetate or chloride but react with *bis*-acetylacetonato cobalt(II) dihydrate leading to the formation of mixed Schiff base-acetylacetonone complexes of both cobalt(II) and cobalt(III). Acetylacetonone and other β-dicarbonyl compounds constitute a prototropic system with interesting properties enabling them to coordinate as the bidentate monoanion and in other ways^{6,7}. With a view to ascertain the mode of coordination of both the Schiff bases and

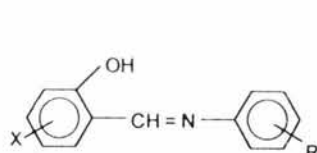
acetylacetonone, the structural determination of one of the cobalt(III) complexes has been carried out.

Materials and Methods

All the chemicals were of reagent grade and used as purchased. Solvents were dried and distilled before use. *bis*-Acetylacetonatocobalt(II) dihydrate, Co(acac)₂·2H₂O was prepared by the literature method⁸. Silica gel-60 which was dried at 140°C was used for chromatographic separations. Microanalyses of C, H and N were performed on Perkin-Elmer-2400 Series II CHN analyser and cobalt was estimated spectrophotometrically. Electronic spectra were recorded in methanol solution on Shimadzu MPS - 2000 UV-VIS spectrophotometer. Infrared spectra (as KBr pellets) were recorded on Perkin-Elmer Paragon 1000 spectrometer. Magnetic susceptibilities were measured on EG and G par vibrating sample magnetometer with Hg[Co(SCN)₄] as standard. Mass spectra (EI - MS, FAB - MS) and ¹H - NMR spectra (in CCl₄ or *d*₆ - acetone) were respectively recorded on JEOL D - 300, JEOL SX - 102 and Varian EN 360 spectrometers.

Syntheses of Schiff bases

HL' : Salicylaldehyde (1.22 g., 10 mmol) diluted



R	X
HL'; 4-COCH ₃	H
HL''; 3-COCH ₃	H
HL'''; 4-COCH ₃	5-Br

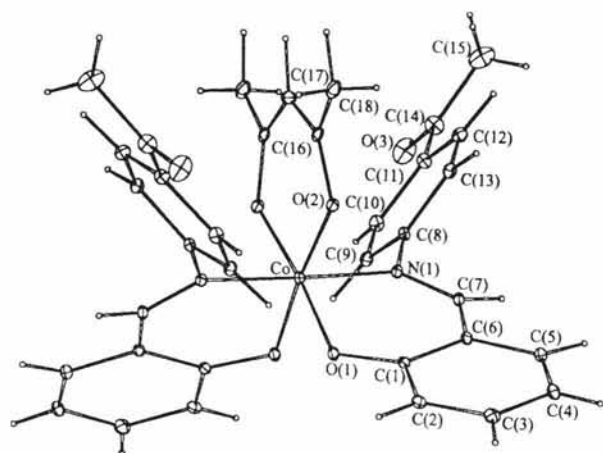


Fig. 1—ORTEP view of $[\text{Co}(\text{L}')_2(\text{acac})]$ (**1**) with atom numbering scheme.

with 10 ml ethanol was added dropwise to 30 ml ethanolic solution of 4-aminoacetophenone (1.34 g., 10 mmol). The mixture was refluxed for 1 h and kept cooled at -5°C . Yellow needle shaped crystals which separated out, were collected, washed with ethanol, diethylether and dried *in vacuo*. Yield, 2.0 g. (85%); m.p., 83°C . Found : C, 75.19; H, 5.53; N, 5.79%. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.30; H, 5.47; N, 5.85%. ^1H -NMR : δ (ppm), 2.7 (3H, s, CH_3); 6.8 - 8.2 (8H, m, $2\text{C}_6\text{H}_4$); 8.6 (1H, s, $\text{CH}=\text{N}$); 12.7 (H, s, OH). IR (KBr) : $\nu(\text{C}=\text{O})$, 1675; $\nu(\text{C}=\text{N})$, 1617; $\nu(\text{C}-\text{O})$, 1281 cm^{-1} . EIMS : m/z , 239 ($=\text{M}^+$).

HL'' : Salicylaldehyde (1.22 g., 10 mmol) and 3 aminoacetophenone (1.34 g., 10 mmol) were reacted and the procedure described for HL' was followed. Yield, 1.91g. (80%); m.p., 65°C . Found : C, 75.40; H, 5.51; N, 5.81%. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.30; H, 5.47; N, 5.85%. ^1H -NMR : δ (ppm), 2.6 (3H, s, CH_3); 6.7 - 8.2 (8H, m, $2\text{C}_6\text{H}_4$); 8.5 (1H, s, $\text{CH}=\text{N}$); 12.8 (H, s, OH). IR(KBr) : $\nu(\text{C}=\text{O})$, 1680; $\nu(\text{C}=\text{N})$, 1618; $\nu(\text{C}-\text{O})$, 1271 cm^{-1} . EIMS : m/z , 239 ($=\text{M}^+$).

HL''' : 5-Bromosalicylaldehyde (2.01g., 10 mmol) and 4-aminoacetophenone (1.34g.) were reacted and the method described for HL' was followed. Yield, 2.28g (72%); m.p., 156°C . Found : C, 56.38; H, 3.77; N, 4.32%. Calcd. for $\text{C}_{15}\text{H}_{12}\text{BrNO}_2$: C, 56.62; H, 3.80; N, 4.40%. ^1H -NMR : δ (ppm), 2.6 (3H, s, CH_3), 6.8-8.1 (7H, m, C_6H_3 , C_6H_4); 8.9 (1H, s, $\text{CH}=\text{N}$); 12.8 (H, s, OH) IR(KBr) : $\nu(\text{C}=\text{O})$, 1674; $\nu(\text{C}=\text{N})$, 1618; $\nu(\text{C}-\text{O})$, 1272 cm^{-1} . EIMS : m/z , 319 ($=\text{M}^+$).

Syntheses of mixed ligand complexes

$[\text{Co}(\text{L}')_2(\text{acac})]$ (**1**) and $[\text{Co}(\text{L}')(\text{acac})]$ (**2**) : $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ (1.19g., 4 mmol) dissolved in 25 ml

Table 1—Crystal data for complex (**1**)#

Formula	$\text{C}_{35}\text{H}_{31}\text{N}_2\text{O}_6\text{Co}$
Colour	Dark green
Formula weight	634.54
Crystal system	Monoclinic
Space group	$\text{C}2/c$
$a(\text{\AA})$	25.756(5)
$b(\text{\AA})$	8.968(2)
$c(\text{\AA})$	13.827(3)
$\beta(^\circ)$	107.71(1)
$V(\text{\AA}^3)$	3042(1)
Z	4
Radiation ($\lambda, \text{\AA}$)	$\text{MoK}\alpha$ (0.71073)
$F(000)$	1320
$\mu(\text{mm}^{-1})$	0.614
$D_c(\text{g cm}^{-3})$	1.385
Crystal size (mm)	0.40×0.30×0.25
θ range ($^\circ$)	2.5< θ <25
Unique reflections	2521
Observed reflections	1845
$[I>2\sigma(I)]$	
$R1^a, \omega R2^b$	0.0498, 0.1072
Weighting parameters (A,B)	0.0642, 0.0
Goodness-of-fit (d_s)	1.047
Maximum Δ , e.s.d.	0.092
Final $\Delta \rho$, max/min ($\text{e}\text{\AA}^{-3}$)	0.564/-0.326

$$^a R1 = \frac{\sum |F_o| - |F_c|}{\sum F_o}$$

$$^b \omega R2 = \frac{[\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{1/2}}$$

$$c_w = 1 / [\sigma^2(F_o^2) + (AP)^2 + BP], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

$$d_s = [\sum \{w(F_o^2 - F_c^2)^2\} / (N - P)]^{1/2}, \text{ where } N \text{ is the number of data and } P \text{ is the total number of parameters refined.}$$

#Estimated standard deviations (esd) of the last digit are in parentheses.

ethanol was added to 25 ml ethanolic solution of HL' (1.91g., 8 mmol). The mixture was stirred at room temperature for 2 h followed by reflux for 3 h. It was filtered hot and the filtrate on reducing the volume to ~10 ml and keeping at -5°C did not yield any solid. The solution was then subjected to column chromatography on a silica gel column (1.5 × 50 cm) and eluted with ethanol. The green coloured first fraction, on removal of the solvent and washing with diethylether and drying *in vacuo*, yielded the compound (**1**) as dark green solid. It was recrystallised from methylene chloride - *n*-hexane (3:1, v/v). Yield, 0.69g. (27%); m.p., 234°C (dec.). Found : C, 66.29; H, 5.02; N, 4.37; Co, 9.18%. Calcd. for $\text{C}_{35}\text{H}_{31}\text{N}_2\text{O}_6\text{Co}$: C, 66.25; H, 4.92; N, 4.41; Co, 9.29%. EIMS : m/z , 634 ($=\text{M}^+$). The dark coloured fraction, obtained as the middle fraction, on evaporation of the solvent and washing with diethylether and drying *in vacuo*, yielded the compound (**2**) as pale green solid. It was recrystallised

Table 2—Selected bond distances (Å) and angles (°) in complex (1)#

Co-O(1)	1.884(2)	C(1)-C(6)	1.417(5)
Co-O(2)	1.891(2)	C(6)-C(7)	1.417(5)
Co-N(1)	1.954(3)	C(11)-C(14)	1.477(5)
O(1)-C(1)	1.312(4)	C(14)-O(3)	1.206(5)
O(2)-C(16)	1.271(5)	C(14)-C(15)	1.481(8)
N(1)-C(7)	1.300(4)	C(16)-C(17)	1.395(5)
N(1)-C(8)	1.428(4)	C(16)-C(18)	1.489(6)
O(1)-Co-O(2)	87.9(1)	Co-O(2)-C(16)	124.5(3)
O(1)-Co-O(2) [†]	175.2(1)	Co-N(1)-C(7)	121.4(2)
O(1)-Co-N(1)	94.3(1)	Co-N(1)-C(8)	121.9(2)
O(1)-Co-N(1) [†]	87.1(1)	C(7)-N(1)-C(8)	116.7(3)
O(1)-Co-O(1) [†]	88.9(2)	C(11)-C(14)-O(3)	121.0(5)
O(2)-Co-N(1)	89.5(1)	C(11)-C(14)-C(15)	120.1(5)
O(2)-Co-N(1) [†]	89.1(1)	C(15)-C(14)-O(3)	118.9(5)
O(2)-Co-O(2) [†]	95.5(2)	C(2)-C(16)-C(17)	124.4(4)
N(1)-Co-N(1) [†]	178.0(2)	O(2)-C(16)-C(18)	115.6(5)
Co-O(1)-C(1)	124.3(2)	C(17)-C(16)-C(18)	120.0(5)

i=-x,y,-z+1/2

[†]Esd values of the last digit are in parenthesesTable 3—Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (1). U(eq) is defined as one third of the trace of the orthogonalised Uij tensor.[#]

	x	y	z	U (eq)
Co	0	2863(1)	2500	37(1)
O1	-505(1)	1364(3)	2543(2)	44(1)
O2	-517(1)	4281(3)	2636(2)	46(1)
N1	340(1)	2902(3)	3970(2)	37(1)
C1	-690(1)	1135(4)	3316(2)	39(1)
C2	-1182(2)	364(4)	3153(3)	49(1)
C3	-1381(2)	36(5)	3950(4)	59(1)
C4	-1096(2)	449(5)	4940(3)	57(1)
C5	-618(2)	1169(5)	5116(3)	50(1)
C6	-403(1)	1550(4)	4326(3)	39(1)
C7	104(2)	2305(4)	4583(3)	42(1)
C8	852(1)	3619(4)	4425(2)	39(1)
C9	1328(2)	3142(5)	4239(3)	49(1)
C10	1808(2)	3818(5)	4712(3)	54(1)
C11	1847(1)	5003(5)	5387(3)	51(1)
C12	1367(2)	5488(5)	5547(3)	53(1)
C13	879(2)	4817(5)	5072(3)	48(1)
C14	2385(2)	5675(6)	5896(4)	74(1)
C15	2430(3)	6942(9)	6604(8)	117(3)
C16	-475(2)	5679(5)	2531(2)	53(1)
C17	0	6398(7)	2500	60(2)
C18	-978(3)	6559(8)	2437(4)	81(2)
O3	2794(1)	5186(5)	5763(3)	114(1)

from methylene chloride - *n*-hexane (4:1, v/v). Yield, 0.86g. (54%); m.p., 210°C(dec.). Found : C, 60.14; H, 4.73; N, 3.42; Co, 14.81%. Calcd. for $C_{20}H_{19}NO_4Co$: C, 60.61; H, 4.83; N, 3.54; Co, 14.87%. μ_{eff} , 4.24 BM (298°K). EIMS : m/z, 396 (= M^+).

[Co(L'')₂(acac)] (3) and Co(L'')(acac)] (4) : Co(acac)₂·2H₂O (1.19g., 4 mmol) and HL'' (1.91g., 8 mmol) were reacted under the same condition and

processed as stated above. The first fraction yielded the compound (3) as a dark green solid. Yield 0.64g (25%); m.p., 226°C(dec.). Found : C, 66.15; H, 4.96; N, 4.33; Co, 9.21%. Calcd. for $C_{35}H_{31}N_2O_6Co$: C, 66.25; H, 4.92; N, 4.41; Co, 9.29%. EIMS : m/z, 634 (= M^+).

The middle fraction yielded the compound (4) as an yellowish green solid. Yield, 0.91g (57%); m.p.,

214°C(dec.). Found : C, 60.22; H, 4.71; N, 3.47; Co, 14.77%. Calcd. for $C_{20}H_{19}NO_4Co$: C, 60.61; H, 4.83; N, 3.54; Co, 14.87%. μ_{eff} , 4.32 BM (298°K). EIMS : m/z , 396 (= M^+).

$[Co(L''')_2(acac)]$ (5) and $[Co(L''')(acac)]$ (6): $Co(acac)_2 \cdot 2H_2O$ (1.19 g., 4 mmol) and HL''' (2.55g, 8 mmol) were reacted under the same condition and processed as stated above. The first fraction yielded the compound (5) as a dark green solid. Yield, 0.77g (24%); m.p., >300°C. Found: C, 52.92; H, 3.61; N, 3.49; Co, 7.51%. Calcd. for $C_{35}H_{28}Br_2N_2O_6Co$: C, 53.12; H, 3.57; N, 3.54; Co, 7.45%. FAB-MS : m/z , 792(= M^+); 793 (= M^++1). The middle fraction gave the compound (6) as a brownish green solid. Yield, 1.03g (54%); m.p., >300°C. Found: C, 50.66; H, 3.84; N, 2.86; Co, 12.32%. Calcd. for $C_{20}H_{18}BrNO_4Co$: C, 50.55; H, 3.82; N, 2.95; Co, 12.40%. μ_{eff} , 4.19 BM (298°K). EIMS : m/z , 475 (= M^+); 476 (= M^++1).

X-ray diffraction structural study of (1)

Single crystals suitable for X-ray structure analysis were obtained by recrystallisation of (1) from methylene chloride - *n*-hexane (3:1, v/v). A single crystal of (1) was mounted on an Enraf - Nonius CAD-4 diffractometer. Lattice parameters were determined by the least squares refinement of the angular settings of 25 well-centred reflections. The crystal data are summarised in Table 1. Intensity data were collected using MoK_{α} radiation ($\lambda=0.71073 \text{ \AA}$) with ω - 2θ scan mode. Three control reflections monitored at regular intervals during the X-ray exposures indicated no significant variation in the intensities. Data were corrected for Lorentz and polarisation effects. An empirical absorption correction⁹ based on ψ scan was applied ($T_{\text{min}}/T_{\text{max}}$, 0.805/0.926). The structure was solved by the heavy atom method and refined through full matrix least-squares calculations (SHELXL 93). Anisotropic refinements were carried out for all non-hydrogen atoms. The hydrogen atoms located from the difference Fourier maps were refined isotropically. All calculations were carried out using SHELXS 86¹⁰, SHELXL 93¹¹, PARST 95¹² and ORTEP II¹³ programs. Selected bond lengths and angles are listed in Table 2. Final atomic coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms are given in Table 3.

Results and Discussion

Reactions leading to the syntheses of mixed ligand complexes were slow and the use of aerielly

preoxidised reaction mixtures increases the yield of the cobalt(III) species, the products still contained predominantly the cobalt (II) species. Room temperature magnetic moment values (μ_{eff} , ~4.2 BM) suggest pseudotetrahedral arrangement of ligands around cobalt(II) ion for the complexes (2, 4, 6)¹⁴. The electronic spectra of the complexes showed a strong absorption band at ~275 nm (intra Schiff base ligand $\pi \rightarrow \pi^*$ transition). The absorption bands at ~365 nm (may be assigned as due to the $^1A_{1g} \rightarrow ^1T_{2g}$ transition which probably contain several transitions e.g. metal to ligand ($t_{2g} \rightarrow \pi^*$) and it is known that the acac anion absorb in the same region) and at ~490 nm and ~570 nm (may be assigned to the split components of $^1A_{1g} \rightarrow ^1T_{1g}$ transition) are the typical pseudoctahedral bands¹⁵ observed for the complexes (1, 3, 5). An absorption of weak to moderate intensity was observed at ~615 nm ($^4A_2(F) \rightarrow ^4T_1(P)$ transition) for the complexes (2, 4, 6). IR spectra of the complexes show characteristic ν (C=O) bands at ~1685 cm^{-1} attributable to carbonyl group present in the Schiff bases. The bands at ~1592 cm^{-1} may be attributed to ν (C...O) of the acetylacetonate anion¹⁶. The ν (C=N) bands appearing at ~1614 cm^{-1} show a lowering in absorption by 3 to 4 cm^{-1} and that of ν (OH) (phenolic) for the Schiff bases at ~3480 cm^{-1} disappears on complexation and the ν (C-O) (phenolic) usually observed at ~1280 cm^{-1} is shifted to 1360 - 1320 cm^{-1} in the complexes supporting Schiff base coordination through imine nitrogen and phenolic oxygen¹⁶. The ν (Co-N) and ν (Co-O) bands appeared respectively at ~470 and ~420 cm^{-1} ¹⁷.

X-ray crystallographic analyses¹⁸

The crystal structure of (1) consists of neutral $[Co(L')_2(acac)]$ molecules occupying crystallographic two-fold sites with half of the complex comprising the asymmetric unit. The occupancy factors of Co, C(17) and H(17) were accordingly fixed to 0.5. An ORTEP view of the complex with the atom numbering scheme is shown in Fig. 1. The cobalt atom is octahedrally coordinated in which four ligand oxygen atoms [O(1), O(2), O(1)ⁱ and O(2)ⁱ; $i = -x, y, -z + 1/2$] define an equatorial plane; the two nitrogen atoms [N(1) and N(1)ⁱ] of the L' ligands are in *trans* - axial positions. The essentially planar L' [O(1), N(1), C(1) - C(7)] and the phenyl moiety [C(8) - C(13)] are inclined to the equatorial plane by 78.7(1)° and 41.1(1)° respectively. The dihedral angle between the two

symmetry related L' ligands is $56.6(1)^\circ$, the corresponding value for the two symmetry related phenyl rings being $79.6(1)^\circ$. The six-membered chelate rings formed by the bidentate L' and the acetylacetonate ligands are folded along $O(1)\dots N(1)$ and $O(2)\dots O(2)^i$ lines, the dihedral angles $Co, O(1), N(1)/C(1), C(6), C(7)$ and $Co, O(2), O(2)^i/C(16), C(17), C(16)^i$ being $21.9(3)^\circ$ and $5.5(1)^\circ$ respectively. The $Co - N$ [$1.954(3)A$] and $Co - O$ [$1.884(2)A, 1.891(2)A$] are consistent with the corresponding values observed in similar octahedral $Co(III)$ systems¹⁹. The crystal packing is stabilised by Van der Waal's forces.

Acknowledgement

The authors are thankful to RSIC, IIT, Madras, India and CDRI, Lucknow, India for single crystal X-ray diffractometer facility and for recording the mass spectra. They also thank the UGC, New Delhi, India (fellowship to IB) and the DST, New Delhi, India (grant to RLD).

References

- 1 Williams D R, *An introduction to bio-inorganic chemistry* (Thomas Springfield) 1975.
- 2 Siegel H, Fisher B E & Farkas E, *Inorg Chem*, 22(1983)925.
- 3 Perkins C M, Rose N J & Stenkamp R E, *Inorg chim Acta*, 172(1990)119.
- 4 Bhirud R G & Srivastava T S, *Inorg chim Acta*, 173(1990)121.
- 5 Luo Q, Kong Li, Shen C, Yu S & Lu Q, *Trans met Chem*, 18(1993)583.
- 6 Mehrotra R C, Bohra R & Gaur D F, *Metal diketonates and allied derivatives* (Academic Press, London) 1978.
- 7 Kawaguchi S, *Coord chem Rev*, 70(1986)51.
- 8 Berg E W & Truemper J T, *J phys Chem*, 64(1960)487.
- 9 North A C T, Phillips D C & Mathews F S, *Acta Crystallogr.*, A24(1968)351.
- 10 Sheldrick G M, SHELXS 86, *Acta Crystallogr.*, A46(1990) 467-473.
- 11 Sheldrick G M, *SHELXL 93*, Programm for the refinement of crystal structure, University of Gottingen, Germany (1993).
- 12 Nardelli M, PARST 95, *J appl Crystallogr.*, 29(1996)296.
- 13 Johnson C K, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA(1976).
- 14 Sacconi L, Ciampolini M, Maggio F & Cavaiano F P, *J Am chem Soc*, 84(1962)3246.
- 15 Boucher L J, *Inorg chim Acta*, 7(1972)29; Cozens R J & Murray K S, *Aust J Chem*, 25(1972)911; Lever A B P, *Inorganic electronic spectroscopy* (Elsevier, New York) (1968) 306-314.
- 16 Gruber S J, Harris C M & Sinn E, *J inorg nucl Chem*, 30(1968)1805.
- 17 Percy G C & Thornton D A, *J inorg nucl Chem*, 34(1972) 3357; Chaudhuri P and Order K, *J chem Soc Dalton Trans*, (1990) 1597.
- 18 Further details of structure analyses and the tables for observed and calculated structure factors may be obtained from the authors.
- 19 Ware D C, Denny W A & Clark G R, *Acta Crystallogr*, C53 (1997)1058.