

Complexes of Cobalt(II) Chloro- & Fluoro-acetates with Some Oxygen Donor Ligands

S L CHADHA* & P R SHARMA

Department of Chemistry, Panjab University, Chandigarh 160 014

Received 5 April 1984; revised 29 October 1984; accepted 21 November 1984

Cobalt(II) monochloro-, dichloro-, trichloro- and trifluoro-acetates react with various monodentate oxygen donors to yield solid adducts having 1:1 or 1:2 stoichiometry. The adduct of cobalt(II) trifluoroacetate with α,α' -bipyridyl-N,N-dioxide has 1:1 composition. The complexes have been characterised by elemental analyses, thermogravimetry, conductance, magnetic moments, infrared, and electronic spectral data.

In our earlier communications^{1,2}, we have reported the preparation and characterization of new adducts of Cu(II) haloacetates with some oxygen donor ligands. The present note describes the preparation and characterization of the adducts of Co(II) haloacetates with oxygen donor ligands, viz. pyridine-N-oxide (Py-O), α -, β - and γ -picoline-N-oxides (α -, β - and γ -pic-O) dimethyl sulphoxide (DMSO), triphenylarsine-oxide (TPAsO), dimethylurea (DMU), tetramethylurea (TMU), hexamethylphosphoramide (HMPA), tetrahydrofuran (THF) and α,α' -bipyridyl-N,N'-dioxide(bipy-O₂).

Materials and Methods

Cobalt(II) monohaloacetates

These were prepared by neutralisation of anhydrous cobalt(II) carbonate with the respective haloacetic acid. The products were washed with ethanol/ether and dried at 50°C *in vacuo* for 6-8 hr.

Cobalt(II) dichloroacetate

A solution of dichloroacetic acid in ethanol was treated with excess of cobalt carbonate and the mixture refluxed. Excess of carbonate was filtered off. The filtrate was concentrated *in vacuo* and red solid of the desired composition obtained, washed several times with petroleum ether (40-60°) and finally dried *in vacuo* at 50° for 6-8 hr.

Cobalt(II) trichloroacetate

The aqueous solution of trichloroacetic acid was neutralised with cobalt carbonate, the solution filtered and excess ethanol added to precipitate hydrated cobalt(II) trichloroacetate. The compound obtained was dried *in vacuo* at 50° for 6-8 hr.

Cobalt(II) trifluoroacetate

Cobalt carbonate was refluxed with an ethanolic solution of trifluoroacetic acid, the excess carbonate

filtered off and the solvent evaporated under reduced pressure when anhydrous cobalt(II) trifluoroacetate was obtained.

All the Co(II) haloacetates gave satisfactory elemental analyses and their purities were further confirmed by spectroscopic data.

Preparation of adducts

The complexes of cobalt(II) monochloro-, dichloro-, trichloro and trifluoro-acetates with the ligands, viz. ureas, amine oxides, hexamethylphosphoratriamide, triphenylarsine oxide, dimethyl sulphoxide and tetrahydrofuran were prepared by dissolving the metal haloacetate in excess of the ligand in case it is a liquid or by mixing the methanolic solution of the haloacetate with the ligand or methanolic/chloroform solution of the ligand or by refluxing the solution of the haloacetate with the solid ligand. In some cases the precipitation of the adducts occurred on mixing while in others, dry solvent ether was added to precipitate the adducts. The complexes were washed a number of times with dry ether and dried *in vacuo*.

Physical measurements

Magnetic moments of the complexes were determined by Gouy method, using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Infrared spectra and far infrared spectra of the complexes were recorded on Perkin-Elmer-337, 521 and 621 grating spectrophotometers. Electronic spectra of the complexes were recorded on Specord UV-VIS, Beckmann Du, VSU-2P and SP700A spectrophotometers. Thermogravimetric analysis of some of the complexes was carried out on a Stanton thermobalance. The conductances of the solutions of the complexes were determined on Toshniwal CL 01/0, 2A type conductivity bridge.

Table 1—Colour, Melting Points and Magnetic Moments of Adducts of Cobalt (II) Haloacetates with Oxygen Donor Ligands

Adduct ^a	Colour	m.p. (°C)	μ_{eff} (B.M.)
A. Py-O	Bluish green	125-26(d)	
A. α -Pic-O	Blue	205	4.76
A. β -Pic-O	do	187	4.74
A. γ -Pic-O	do	183-84	
A. TPAsO	do	66-67	4.78
A. DMSO	Sky blue	110	
B. 2DMU	Blue	90-91	4.80
B. PyO	Pink	147	4.72
B. α -Pic-O	do	248	4.73
B. β -Pic-O	do	236,37	4.70
B. γ -Pic-O	do	247	4.70
B. 2HMPA	Blue	290-91(d)	
B. 2THF	Pink	270	4.93
C. α -Pic-O	do	155-60(d)	4.69
D. 2DMU	do	105	5.10
D. 2TMU	do	176-77	
D. α -Pic-O	do	300	4.72
D. β -Pic-O	Light brown	280	
D. Bipy-O ₂	Pink	280	4.93

^aA = Co(CH₂ClCO₂)₂; B = Co(Cl₂CHCO₂)₂; C = Co(Cl₃CCO₂)₂; and D = Co(F₃CCO₂)₂.

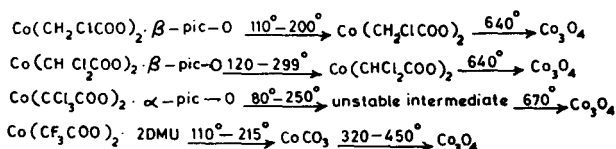
Py-O = pyridine-N-oxide; α -, β -, γ -Pic-O = α -, β -, γ -picoline-N-oxide; DMSO = dimethyl sulphoxide; TPAsO = triphenylarsine oxide; DMU = dimethylurea; HMPA = hexamethylphosphorotriamide; THF = tetrahydrofuran; and Bipy-O₂ = α , α' -bipyridyl-N,N'-dioxide.

Results and Discussion

The analytical data of the adducts corresponded to the composition of the complexes given in Table 1. Cobalt(II) monochloro-, dichloro-, trichloro- and trifluoro-acetates yield stable, blue or pink complexes with DMU, TMU, DMSO, THF, HMPA, TPAsO, α -, β - and γ -picoline-N-oxides (α -, β - and γ -pic-O), pyridine-N-oxide (Py-O) and α , α' -bipyridyl-N,N'-dioxide(bipy-O₂) in non-aqueous media. The adducts with amine oxides have 1:1 stoichiometry whereas with other ligands adducts of 1:2 (metal-ligand) stoichiometry are formed (Table 1), except in the case of cobalt(II) monochloroacetate which forms 1:1 adducts with amine oxides. The complexes are slightly hygroscopic and are freely soluble in methanol or ethanol, while a few of them are fairly soluble in nitromethane. The molar conductance values of these complexes in nitromethane (10^{-3} M) are of the order of 10.1-13.3 ohm⁻¹ cm² mol⁻¹ indicating their covalent behaviour³ in this medium. However the molar conductivities in methanol are of the order of 36.2-50.2 ohm⁻¹ cm² mol⁻¹. This shows dissociation of the adducts in the solvent giving conducting species. The THF adduct of cobalt(II) dichloroacetate has the highest conductivity in methanol. The value required

for univalent electrolyte in methanol⁴ is 120-140 ohm⁻¹ cm² mol⁻¹.

Thermogravimetric studies have been carried out for the complexes, Co(CH₂ClCO₂)₂· β -pic-O, Co(Cl₂CHCO₂)₂· β -pic-O, Co(Cl₃CCO₂)₂· α -pic-O and Co(CF₃CO₂)₂·2DMU. The DTG and TGA data show that they decompose in accordance with proposed Scheme 1.



Scheme 1

The room temperature magnetic moments of the blue adducts (Table 1) lie in the range 4.76-4.90 B.M., suggesting a tetrahedral stereochemistry^{5,6} for these complexes. The magnetic moments of the pink-coloured (1:2) adducts lie in the range 4.86-5.12 B.M. (Table 1), indicating an octahedral geometry^{6,7} for these pink-coloured adducts. However, the 1:1 adduct of cobalt(II) dichloro-, trichloro- and trifluoro-acetates with pyridine-N-oxide, and α -, β - and γ -picoline-N-oxides have magnetic moments between 4.70 and 4.73 B.M. (Table 1). Although the pink colour of these complexes is indicative of their octahedral stereochemistry, the slight decrease in their magnetic moments may be due to the super exchange mechanism operating through bridging oxygen atoms of the ligands^{8,9}.

The absorption spectra and solid reflectance spectra of the blue adducts exhibit one intense band (with extinction coefficient of the order of 200 litre cm⁻¹ mol⁻¹) in the region 16.6-14.0 kK which may be assigned to $^4A_2(F) \rightarrow ^4T_1(P)$ transition. Another weak band close to 8.0 kK corresponding to the transition, $^4A_2(F) \rightarrow ^4T_1(F)$, indicates tetrahedral stereochemistry^{6,10} for these adducts. An absorption band in the region 20.0-16.6 kK (having molar extinction coefficient of the order of 11.0 litre cm⁻¹ mol⁻¹) in the electronic spectra of the pink-coloured complexes may be due to the transition, $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$. Besides, a shoulder and a less intense band (molar extinction coefficient of the order of 2.0 litre cm⁻¹ mol⁻¹) appearing around 16.0 and 8 kK respectively may be assigned to the transitions, $^4T_{1g}(F) \rightarrow ^4A_{2g}$ and $^4T_{1g}(F) \rightarrow ^4T_{2g}$. These observations indicate octahedral geometry^{6,7,11} for the pink-coloured adducts.

Infrared spectra of the complexes (Table 2) indicate that the $\nu(\text{N}-\text{O})$ of amine oxides, $\nu(\text{C}=\text{O})$ of ureas, the $\nu(\text{P}=\text{O})$ of hexamethylphosphorotriamide (HMPA), $\nu(\text{As}=\text{O})$ of triphenylarsineoxide, $\nu(\text{S}=\text{O})$ of DMSO and $\nu(\text{C}-\text{O}-\text{C})$ of THF are present at lower spectral

Table 2—Major Infrared Spectral Frequencies (cm^{-1}) of the Adducts of Cobalt (II) Haloacetates^a

Adduct ^b	$\nu_{\text{as}}\text{OCO}$	$\nu_{\text{s}}\text{OCO}$	$\nu(\text{N}-\text{O})/\nu(\text{C}=\text{O})/\nu(\text{P}=\text{O})/\nu(\text{As}=\text{O})/\nu(\text{S}=\text{O})/\nu(\text{C}-\text{O}-\text{C})$	$\delta(\text{C}-\text{H})/\delta(\text{N}-\text{C}=\text{O})/\nu(\text{P}-\text{N})/\nu(\text{C}-\text{As})/\nu(\text{C}-\text{S})$	$\nu(\text{O} \rightarrow \text{Co})$
A. Py-O	1630m, 1610vs (1570s) ^a	1360vs (1370s)	1180vs (1265vs)	780w (758vs)	
B. Py-O	1642s (1620vs)	1380vs (1450s)	1175s	770s	
A. α -Pic-O	1620vs, 1595sh	1360	1200vs (1245s)	775s (760s)	
B. α -Pic-O	1640vs	1372vs	1200vs	766vs	410w, 390s, 380w, 360w.
C. α -Pic-O	1683vs (1680s)	1360vs (1380vs)	1215vs	776m	
D. α -Pic-O	1700sh, 1670vs (1677vs)	1365vs (1450s)	1203s	770s	350s, 330w, 270w, 255w.
A. β -Pic-O	1617vs, 1595sh	1358s	1204m (1250vs)	768s (745vs)	
B. β -Pic-O	1645vs	1380vs	1164vs	770.	
D. β -Pic-O	1660s	1355s	1210vs	739s	350s, 311w, 295m, 274m.
A. γ -Py-O	1645m, 1610s	1355m	1200s (1255s)	766s (750vs)	
B. γ -Py-O	1645s	1370vs	1210vs	765vs	
D. Bipy-O ₂	1710s	1370vs	1205s, 1660m, 1140s (1262m, 1255s)	783s (759s)	384vs, 295s
B. 2DMU	1662	1355s	1570s (1650m)	765s (722m)	400w, 390w, 378w
D. 2DMU	1700vs	1365vs	1570vs	762	333m, 320m, 285s, 255s
D. 2TMU	1680vs	1350vs	1570s (1650s)	775m (733m)	
B. 2HMPA	1660s	1355s	1152s (1210vs)	786s, 668m (752s, 636ms)	
A. DMSO	1632m, 1601vs	1350s	986s	710s, 670m (696m, 664s)	430m, 360s, 330m, 250m
A. TPAsO	1655, 1615s	1365s	865s (881vs)	477s (497s)	340w
B. 2THF	1640vs	1360s	1020vs, 828m, 818vs (1070vs, 912vs)		432w, 400w, 375w

^(a)Characteristic frequencies of cobalt (II) haloacetates and the ligands are given in parentheses.^(b)A = Co(ClCH₂CO₂)₂; B = Co(Cl₂CHCO₂)₂; C = Co(Cl₃CCO₂)₂; and D = Co(F₃CCO₂)₂.

positions as compared to those in the pure ligands (Table 2) which is in line with the coordination of these ligands through their oxygen atoms¹²⁻¹⁹. The $\nu_{\text{as}}\text{OCO}$ and $\nu_{\text{s}}\text{OCO}$ of pure haloacetates move to higher and lower spectral regions, respectively, in the spectra of the adducts (Table 2). The $\nu_{\text{as}}\text{OCO}$ of the carboxylate group is known to be particularly sensitive to the mode of coordination. $\nu_{\text{as}}\text{OCO}$ lies in the region 1660-1580 cm^{-1} depending on the covalent character of M-O bond. The coordination of ligands to metal enhances the electron density on the metal which in turn increases the covalent character of M-O band between metal and COO group and consequently $\nu_{\text{as}}\text{OCO}$ increases. The bands in the IR spectra of the adducts in far IR region 330-440 cm^{-1} are due to

metal-carboxylate and metal-ligand stretching modes²⁰⁻²²

References

- 1 Paul R C, Makhni H S, Singh P, Chadha S L, *J inorg nucl Chem*, **32** (1970) 3694.
- 2 Paul R C, Sharma P R & Chadha S L, *Indian J Chem*, **15A** (1977) 27.
- 3 Lever A B P, *J Inorg nucl Chem*, **27** (1965) 149.
- 4 Harris C M & Lockyer T N, *J chem Soc*, (1959) 3083.
- 5 Cotton F A & Wilkinson G, *Advanced Inorganic Chemistry*, (Interscience, New York) 1962, 726.
- 6 Graddon D P, Hang K B & Walton E C, *Aust J Chem*, **21** (1968) 121.
- 7 Lever A B P & Ogden D, *J chem Soc (A)*, (1967) 2041.
- 8 Cotton F A & Wilkinson G, *Advanced inorganic chemistry*, (Interscience, New York) 1972, 881.

- 9 Harris C M, Kakot E, Lesser S L & Lockyer T N, *Chem Ind*, (1962) 651.
- 10 Cotton F A, Fout O D, Goodgame D M L & Holm R H, *J Am chem Soc*, **83** (1961) 1780.
- 11 Meek D W, Drago R S & Piper T S, *Inorg Chem*, **2** (1962) 285.
- 12 Karayannis N M, Space A N, Pytlewski L L & Labes M M, *J lesscommon met*, **22** (1970) 117.
- 13 Ahuja I S & Singh R, *Spectrochim Acta*, **30A** (1974) 2055.
- 14 Paul R C, Makhni H S, Singh P & Chadha S L, *J lesscommon met*, **17** (1969) 437.
- 15 Kumar Dass V G & Kitching W, *J organomet Chem*, **13** (1968) 523.
- 16 Paul R C, Sharma P R, Subbiah L & Chadha S L, *Indian J Chem*, **14A** (1976) 866.
- 17 Clark J P, Longford V M & Wilkins C J, *J chem Soc (A)*, (1967) 792.
- 18 Clark R J H, Lewis J, Machin D J & Nyholm R S, *J Chem Soc*, (1963) 379.
- 19 Lever A B P, Lewis J & Nyholm R S, *J chem Soc*, (1962) 5262.
- 20 Briggs E M & Hill A E, *J chem Soc*, (1969) 1835.
- 21 Kakuti Y, Kida S & Quagliano J V, *Spectrochim Acta*, **19** (1963) 201.
- 22 Bernary C V & Weber S H, *Inorg Chem*, **7** (1969) 283.