Inorganica Chimica Acta, 105 (1985) 223–226

Synthesis and Characterization of Co(III) Complexes of 2-Pyridinecarboxaldehyde Thiosemicarbazone

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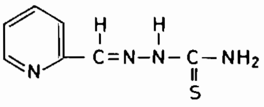
Received April 29, 1985

Abstract

Cobalt(III) complexes of 2-pyridinecarboxaldehyde thiosemicarbazone with an appropriate anion such as Cl^-, NCS^-, NO_3^- and CN^- were prepared. Elemental analysis, magnetic measurements and EPR data, molar conductances and infrared spectra of these complexes were employed to characterize the complexes. 2-pyridinecarboxaldehyde thiosemicarbazone is coordinated to Co(III) ion in a 2:1 ratio. The anions associate with the high spin cobalt(III) in the polycrystalline complexes. We confirmed by titrimetric analysis using standard thiosulphate that cobalt is in a tripositive state in all the complexes.

Introduction

The synthesis of several thiosemicarbazones from 2-pyridinecarboxaldehyde and related compounds have recently been carried out [1]. The 2-pyridinecarboxaldehyde thiosemicarbazones have been found to be more effective in reducing tissue iron levels than the deferoxamine, which is used for removing excess iron accumulated in tissues of patients with Cooley's anemia [2, 3]. The 2-pyridinecarboxaldehyde thiosemicarbazone behaves as a tridentate ligand with two nitrogens and one sulphur as donor atoms. The iron(II) complexes of 2-pyridinecarboxaldehyde thiosemicarbazone in the ratio 1:2 were isolated by Antholine and co-workers [4, 5], and were found to have a substantial inhibitory effect against tumor cells. We report in this paper the synthesis and characterization of several new Co(III) complexes of 2-pyridinecarboxaldehyde thiosemicarbazone (compound Z) in the ratio of 1:2 with five different anions.



Compound Z

Experimental

The ligand, 2-pyridinecarboxaldehyde thiosemicarbazone (Z) (abbreviated as PT-H and its anion −1 charge as PT) was prepared by a standard method [6].

The synthesis of the complexes $Co(PT)_2X$ (X = Cl, NCS, NO_3, N_3, CN) followed the same procedure and details for one reaction are given below. Other reactions are summarized in Table I.

Preparation of $Co(PT)_2Cl$

$CoCl_2$ (1 mmol) was dissolved in water containing 20 ml of 0.5 M HCl. The solution was mixed with the solution of the ligand (2 mmol) in ethanol. The mixed solution was stirred for 3 h. The solution was concentrated at room temperature. Brown crystals were obtained, washed with cold methanol, and dried over $CaCl_2$.

Physical Measurements

For the magnetic measurements, the Gouy method was employed, with $Hg[Co(NCS)_4]$ used as the standard. Diamagnetic corrections were also applied using Pascal's constants from the literature [7]. The electron paramagnetic resonance (EPR) spectra of polycrystalline samples were recorded on a Varian E-112 Spectrometer (X-band) using TCNE (g = 2.00277) as a standard.

Electronic absorption spectra of the complexes and the ligand were recorded on a Perkin-Elmer model 402 spectrophotometer in dimethylformamide

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TABLE I. Reaction Conditions and Analytical Data.

$CoCl_2$	Ligand PCT	Anion	Solvent	Compound	Reaction time	Analytical data (%)[a]				
						C	H	N	S	Cl
1.0 mmol	2.0 mmol	KNCS 25 mmol	EtOH	$Co(PT)_2NCS$	3 h	37.68 (37.73)	2.66 (3.35)	25.95 (26.42)	19.64 (20.12)	
1.0 mmol	2.0 mmol	0.5 M HNO_3 20 ml	Water HCl/NH_4OH	$Co(PT)_2NO_3$	4 h	34.96 (35.07)	2.97 (2.92)	26.41 (26.30)	12.85 (13.36)	
1.0 mmol	2.0 mmol	NaN_3 2 mmol	MeOH	$Co(PT)_2N_3$	1 h	37.01 (36.60)	3.28 (3.05)	33.56 (33.65)	13.78 (13.94)	
1.0 mmol	2.0 mmol	KCN 2 mmol	MeOH	$Co(PT)_2CN$	2 h	40.42 (40.44)	2.86 (3.40)	28.18 (28.44)	13.84 (14.38)	
1.0 mmol	2.0 mmol	0.5 HCl 20 ml	EtOH	$Co(PT)_2Cl$	3 h	37.87 (37.13)	3.04 (3.07)	23.46 (23.46)	14.43 (14.54)	7.35 (7.52)

[a] Calculated values in parentheses.

(DMF) in the range 300 to 800 nm. Infrared spectra of the complexes and the ligand were recorded on a model spectrophotometer in Nujol mull or KBr pellet, in the range 4000–200 cm^{-1}.

Molar conductances of the complexes in DMF solution at room temperature (after appropriate incubations) were measured with a platinum cell (cell constant O = 0.0843 cm^{-1}).

TABLE II. Molar Conductances of $Co(PT)_2X$[a] in DMF at 28 °C.

Complexes	Molar conductances in mhos cm^2 mol^{-1} at room temperature[b]	
	After 1 h incubating at room temperature	After 2 h incubating at 50 °C
$Co(PT)_2Cl$	59.5	69.0
$Co(PT)_2NCS$	134.3	138.5
$Co(PT)_2NO_3$	98.3	103.2
$Co(PT)_2N_3$	49.1	74.1
$Co(PT)_2CN$	82.5	88.0

[a] $X^- = Cl^-, NCS^-, NO_3^-, N_3^-$ and CN^-. [b] Molar concentration = 10^{-3} M.

TABLE III. Magnetic Moment and EPR Data of Polycrystalline $Co(PT)_2X$.[a]

Complex	Magnetic moment μ_{eff} (BM) (298 K)	EPR data g (77 K)
$Co(PT)_2Cl$	3.89	Diamagnetic
$Co(PT)_2NCS$	3.93	Diamagnetic
$Co(PT)_2NO_3$	3.88	3.861
$Co(PT)_2N_3$	3.87	3.782
$Co(PT)_2CN$	3.86	3.881

[a] $X = Cl^-, NCS^-, NO_3^-, N_3^-$ and CN^-.

Results and Discussion

Complexes of the formula $Co(PT)_2X$ (where X^- = Cl^-, NCS^-, NO_3^-, N_3^- and CN^-) were synthesized by the interaction of $CoCl_2$ and 2-pyridinecarboxaldehyde in a ratio of 1:2 in a methanol–water mixture in the presence of an excess of the appropriate anion. Complexes are insoluble in a variety of solvents such as sodium hydroxide, ether, benzene, carbon tetrachloride and chloroform, but are slightly soluble in acetone. They are soluble in water and methcoal, and highly soluble in DMF and dimethylsulphoxide.

Molar Conductivity Measurements

The molar conductances, Table II, of the complexes vary from 49.1 to 134.3 mhos cm^2 mol^{-1} after one h incubation at room temperature, and from 69.0 to 138.5 mhos cm^2 mol^{-1} after 24 h incubation at 50 °C. These variations are indicative of some complexes being weakly associated in DMF [8]. The degree of association is also dependent on the incubation period.

Magnetic Measurements

The magnetic moments (μ_{eff}) of the polycrystalline complexes (calculated from their magnetic susceptibility data, obtained at room temperature) are given in Table III. They vary from 3.86 to 3.93 BM. These values can be rationalized in terms of high spin cobalt(III) complexes [9]. The g values of these polycrystalline complexes were evaluated from their EPR data obtained at liquid nitrogen temperature, and are presented in Table III. The azido and nitrato complexes exhibit broad symmetrical signals which are explicable in terms of spin-spin relaxation, probably via dipolar interactions [10]. The cyano complex has a broad asymmetric signal which may be due to concentration broadening of the signal of high-spin Co(III) complex with axial or rhombic symmetry. The chlorido and thiocyanato complexes are essentially diamagnetic at liquid nitrogen temperature. This may be due to spin pairing *via* exchange coupling, through the anions, between two high-spin Co(III) ions [11]. Consequently most of the anions of the complexes interact with the Co(III) ion.

Electronic Spectra

After 2 to 3 h of incubation, the electronic absorption maxima of the complexes and the ligand were recorded in DMF (see Table IV). The dependence of absorption maxima (number, position and extinction coefficient ϵ_{max}) on the nature of anions obviously indicates that the anions are associated to a different extent in the coordination sphere of the Co(III) complexes in solutions, as confirmed by the conductivity data summarized in Table II. Thus the absorption bands observed in the Co(III) complexes can be tentatively assigned. The intense bands above 30,000 cm^{-1} are assigned π–π* transitions. The band at 22,232 cm^{-1} in the azide and thiocyanate derivatives may be assigned as charge transfer, probably d–π*, and a band centred around 17,000 cm^{-1} in the cyanide and nitrate derivatives may be due to d–d transition [12].

TABLE IV. Electronic Absorption Maxima of Co(PT)$_2$X^a in DMF.

Complex	ϵ_{max} (cm^{-1})	ϵ_{max}
ligand PCT	30303	25460
Co(PT)$_2$Cl	30124	48884
Co(PT)$_2$NCS	30013	33240
	22232	180
Co(PT)$_2$NO$_3$	30524	27988
	17241	418
Co(PT)$_2$N$_3$	28581	4100
	22232	2555
Co(PT)$_2$CN	31270	17635
	23815	5372
	16959	480

^{a}X = Cl$^-$, NCS$^-$, NO$_3$$^-$, N$_3$$^-$, and CN$^-$.

Infrared Spectra

The spectra of the free ligand PT and a typical IR spectra of compound Co(PT)$_2$NCS are given in Table V.

For convenience we will discuss only the selective infrared bands. The highest frequency band of the 2-pyridinecarboxaldehyde thiosemicarbazone at 3425 cm^{-1} can be assigned to the asymmetric ν(N–H) vibration of the terminal NH$_2$ group. The other bands at 3250 and 3140 cm^{-1} may be due to the symmetric ν(N–H) vibrations of the imino and amino groups. The C=N and C=C stretching vibrations are partly overlapping and the band at 1618 cm^{-1} (doublet) is assigned to them. The band at 1585 cm^{-1} is assigned to δ(N–H) vibration of NH$_2$ group [13]. The band at 780 cm^{-1} may be assigned to ν(C=S) + ν(C–N) vibrations [14]. The bands centred at 610 and 423 cm^{-1} in the free ligand are assigned to in plane pyridine ring deformation and out of planc ring deformation respectively [15].

TABLE V. Infrared Spectra of PT and Co(PT)$_2$NCS.

PT	Co(PT)$_2$NCS	Assignments
3425 s	3425 br	asy ν(N–H) terminal
3140 s		sym νN–H
	3040 vs	νNCS
1618 s	1645 s	νC=N
1585 s	1585 s	δ(N–H) of NH$_2$
780 vs		νC=S + ν(C–N)
610 s	625 s	i.p. def. pyridine ring
423	435 s	o.p. def. pyridine ring

Some infrared absorption bands in the range 3425 to 3140 cm^{-1} in the Co(III) complexes are broad, due to hydrogen bonding. One prominent band at 3140 cm^{-1} disappeared completely, due to enolization of the C=S group on complex formation. The C=N and C=C stretching frequencies are shifted from 1618 cm^{-1} (doublet) to 1645 cm^{-1} (doublet) on complex formation. This shift of 27 cm^{-1} is probably due to the involvement of the C=N group on complex formation. The δ(N–H) vibration of NH$_2$ group is not shifted, because it is not involved in bonding. The ν(C=S) + ν(C–N) vibration at 780 cm^{-1} of the free ligand disappears in the complexes. This implies that the enolized form of C=S is involved in the bonding. The band at 610 cm^{-1} in the free ligand is shifted to 625 cm^{-1} and the other band at 423 cm^{-1} is shifted to 438 cm^{-1} on complex formation. This indicates that the nitrogen atom of the pyridine group is involved in complex formation [15].

The nitrate ion may be coordinated to Co(III) in the nitrate complex because the infrared bands in the ionic NO$_3^-$(KNO$_3$) were absent [15]. The metal–chlorine frequency usually shows up between 300 and 200 cm^{-1}. In the chloro-complex, this appears around 400 cm^{-1}. The ν_a(NNN) and ν_s(NNN) stretching vibrations of the azide group were observed at 2050 and 1325 cm^{-1} respectively, as compared to the ionic sodium azide values of 2128 and 1358 cm^{-1} [16]. This is explicable in terms of coordination of azide to the Co(III) in the complex. The ν(CN) vibration of thiocyanate group was observed at 2040 cm^{-1} in the thiocyanato complex, as compared to the ionic thiocyanate value of 2053 cm^{-1}. This can be explained in terms of the nitrogen atom of the thiocyanate being coordinated to Co(III) in the thiocyanato derivative. The ν(CN) vibration of the cyanide group was observed at 2040 cm^{-1}, as compared to 2080 cm^{-1} observed in the ionic cyanide ions. The low frequency shift can be explained in terms of coordination of cyanide ions, to Co(III) in the cyano complex [15].

Complexes of Co(III) of the formula $Co(PT)_2X$ where $X^- = Cl^-, NCS^-, NO_3^-, N_3^-$ and CN^- have been synthesized. Some of the anions of the Co(III) complexes are associated both in the solid state and in DMF solution; the extent of association is dependent on the nature of the anion.

Acknowledgement

We thank Professor J. J. Turner and Dr. D. B. Sowerby of the Department of Chemistry, Nottingham University, U.K., for the provision of research facilities.

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