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Iron(III) Complexes of Pentadentate Ligands

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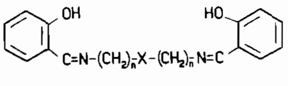
Iron(III) complexes of pentadentate ligands derived from salicyaldehyde and 2,2′-bis(aminoethyl)sulfide, diethylenetriamine and 3,3′-bis(aminopropyl)amine have been prepared and characterized employing elemental analysis, infrared–visible–ultraviolet spectra, mass spectra and magnetic susceptibility measurements. Complexes of formula [Fe(Ligand)] were isolated in each case. The structure of the materials is postulated to be five or six coordinate depending upon whether the secondary amine or thioether linkage is bound to the iron(III) ion. Conductivity data reveal the chloride ion to be coordinated.

Introduction

Iron(III) complexes employing pentadentate ligands have not been studied extensively. Previous reports of complexes between iron(III) and bidentate N-substituted salicylaldimines have described the bis and tris derivatives $[Fe(SAL–NR)_{2\text{ or }3}]^{+1\text{ or }0}$ where R is an alkyl or aryl group[2]. Quadridentate ligands of the type bis(salicylaldehyde)ethylenedimine form related complexes (i.e. Fe(SALEN)X) where X = Cl^-, Br^- and NO_3^- together with the bridged oxo derivative, $[Fe(SALEN)]_2O$.[3]

In this paper we describe the synthesis and characterization of chloro derivatives of iron(III) with three pentadentate ligands derived from salicylaldehyde and (1) 2,2′-bis(aminoethyl)sulfide hereafter referred to as SALDAES(I), (2) diethylenetriamine hereafter referred to as SALDIEN(II) and (3) 3,3′-bis(aminopropyl)amine hereafter referred to as SALDPT(III).



I n = 2 X = S
II n = 2 X = N–H
III n = 3 X = N–H

Experimental

Materials

2,2′-Bis(aminoethyl)sulfide (DAES) was donated by the Dow Chemical Company. The other two polyamines, diethylenetriamine(DIEN) and 3,3′-bis(aminopropyl)amine (DPT), and salicylaldehyde were of reagent grade and obtained from Aldrich Chemical Company. Anhydrous iron(III) chloride was prepared in a tube furnance by the reaction of iron filings with chlorine at 400° C. The product was stored in a sealed tube. SALDAES was prepared as previously described[4].

Preparation of Fe(SALDAES)Cl

A solution containing 300 ml of ethanol, 4.5 ml triethylorthoformate, and 2.02 g triethylamine was prepared, stirred and heated. When warm, 3.28 g (0.01 moles) of SALDAES was added and allowed to dissolve. A nitrogen flow was initiated through the solution. Another solution containing 60 ml of ethanol and 1.62 g (0.01 moles) of $FeCl_3$ was added dropwise, refluxing was begun and continued for 1 hour. After being cooled overnight, dull-red crystals were filtered by suction under nitrogen. These crystals were dried for 12 hours *in vacuo* at 100° C.

Preparation of Fe(SALDPT)Cl

A solution containing 300 ml of ethanol, 8.5 g (0.076 moles) of triethylamine and 5 ml of triethylorthoformate was prepared and warmed. 9.27 g (0.076 moles) of salicylaldehyde was added. Stirring was begun and a nitrogen flow was initiated through the solution. 4.98 g (0.038 moles) of DPT dissolved in 60 ml of ethanol was added dropwise to the solution. The addition funnel was washed with ethanol and 6.1 g (0.038 moles) of $FeCl_3$ dissolved in 60 ml of ethanol was added dropwise. After refluxing for 90 minutes, the solution was cooled overnight and filtered by suction under nitrogen. The experiment yielded coal-black crystals which were dried at 100° C *in vacuo* for 12 hours.

Preparation of Fe(SALDIEN)Cl

A solution containing 4.09 g (0.09 moles) of triethylamine and 5 ml of triethylorthoformate dissolved in 250 ml of ethanol was prepared. 4.88 g (4.04 moles) of salicylaldehyde was added. Stirring, heating and a nitrogen flow were begun. 2.06 g (0.02 moles) of DIEN was dissolved in 40 ml of ethanol and the solution was added dropwise to the salicylaldehyde solution. The addition funnel was washed with ethanol, and 3.29 g (0.02 moles) of $FeCl_3$ dissolved in 60 ml of ethanol was added dropwise to the solution. Refluxing was continued for 1 hour. The solution was allowed to cool overnight and yielded purple-black crystals which were isolated and dried as described previously.

Physical Measurements

Infrared adsorption spectra in the region 5000–400 cm^{-1} were determined employing a Nujol or hexachlorobutadiene mull technique with a Perkin–Elmer Model 621 grating spectrophotometer.

Ultraviolet–visible–near infrared spectra at room temperature were obtained using a Cary 14 recording spectrophotometer. Diffuse transmittance spectra were obtained using Nujol mulls supported on Whatman No. 1 filter paper.[5]

Magnetic susceptibility data were obtained at room temperature by the Faraday method using mercury (II)tetrathiocyanatocobaltate(II) and tris(ethylenediamine)nickel(II) thiosulfate as the calibrants. Diamagnetic corrections were made employing Pascal's constants.[6]

Molar conductances were measured using a Barnstead Model PM-70CB conductivity bridge and a cell with a constant of 1.50 cm^{-1}.

Mass spectra were obtained on a Hitachi–Perkin–Elmer RMU–7 double focusing mass spectrometer using a solid inlet probe. Analyzer tube and ion source pressures of less than 10^{-6} torr were employed. Where necessary mass to charge ratios were calibrated with perfluorokerosene. The ionizing electron energy was 50 e.v. The inlet and source temperatures were approximately 280° C and 230° C respectively.

Elemental analyses were performed in this laboratory using a Perkin–Elmer Model 240 carbon, hydrogen nitrogen analyzer.

Results and Discussion

All three compounds, Fe(SALDAES)Cl, Fe(SALDPT)Cl and Fe(SALDIEN)Cl give well defined, crystalline products which are relatively stable at room temperature. Their decomposition points are, respectively, 213° C, 186° C and 253° C. None of the complexes are very soluble in any solvent, but dilute solutions can be prepared employing acetone, DMF and $CHCl_3$. The analytical data for these three compounds are listed in Table I.

Infrared spectra are similar for each complex and strongly support the suggested formulation. A relatively strong band with an accompanying shoulder is observed at 1630 cm^{-1} for Fe(SALDPT)Cl and Fe(SALDIEN)Cl and at 1620 cm^{-1} in Fe(SALDAES) Cl. This band and shoulder are assigned to a symmetric and asymmetric C=N stretching vibration. Bands at 3260 cm^{-1} for Fe(SALDIEN)Cl and at 3237 cm^{-1} for Fe(SALDPT)Cl are assigned to the secondary nitrogen hydrogen stretching mode. These bands are of medium intensity and surprisingly are quite sharp. The free ligands, H_2SALDIEN and H_2SALDPT, have broad and weak N–H stretching modes at 3305 cm^{-1} and 3255 cm^{-1} respectively. These observations suggest that the secondary amine in each ligand is perhaps weakly coordinated to the iron(III). Support for this argument is obtained from the fact that complexes of formula M^{II}(SALDPT) where M is a divalent first row transition metal ion exhibit a medium–weak sharp band at 3250 cm^{-1} which is assigned to a coordinated N–H stretching vibration.[7] Threedimensional x-ray analysis of Ni(SALDPT) also implies a nickel-secondary amine linkage.[8] The decrease of only 18 cm^{-1} although the charge on the metal is +3 may be accounted for by the smaller size of the trivalent ion when compared with the divalent ion *vide infra.* The data concerning SALDIEN is less straightforward. Nickel(II) complexes of SALDIEN show in the infrared only a very weak broad band indicative of a non-coordinated secondary nitrogen-hydrogen stretch[9]. Akhtar, et. al.[10] have postulated that SALDIEN is not flexible enough to act as quinquedentate ligand in compounds which have a metal to donor atom distance of approximately 2Å. Such is the case with first row

TABLE I. Analytical Data.

	Calculated %			Found %		
	C	H	N	C	H	N
Fe(SALDAES)Cl	51.74	4.35	6.70	52.14	4.33	6.90
Fe(SALDIEN)Cl	53.95	4.78	10.48	54.37	4.89	10.29
Fe(SALDPT)Cl	56.02	5.41	9.80	55.95	5.51	10.00

transition metal compounds. The sharpness and shift of the N–H stretch in Fe(SALDIEN)Cl may be attributed to coordination although crystal packing effects in which the secondary amine is not hydrogen bonded but restricted in some way seems more feasible. The lower N–H stretching frequency for Fe(SALDPT)Cl suggest a more strongly coordinated secondary nitrogen in this complex than in Fe(SALDIEN). Finally a band assignable to an iron(III)–chlorine stretch is also observed in the 380–395 cm^{-1} region in each of the complexes.[11]

Molar conductances measured in $CHCl_3$ reveal the materials to be non-electrolytes. In pyridine and DMF the subject complexes show some dissociation with decreasing concentration which arises as a result of a pyridine or DMF molecule substituting for the chloride ion in the inner coordination sphere of the iron(III).

The mass spectra of each complex exhibited no peak corresponding to the molecular ion; although, the parent minus one chloride ion fragment gave a very intense ion cluster in each case (i.e. $[Fe(SALDPT)]^+$, $[Fe(SALDIEN)]^+$ and $[Fe(SALDAES)]^+$. These data provide good evidence for the proposed composition, and further suggests that dimer formation in the gas phase is an unlikely possibility.

Magnetic susceptibilities measured at four different field strengths are indicative of high spin octahedral or five-coordinate species for Fe(SALDPT)Cl, $\mu_{eff} = 5.92$ B.M., and Fe(SALDIEN)Cl, $\mu_{eff} = 5.86$ B.M.[12,13] The magnetic moment obtained for Fe (SALDAES)Cl, $\mu_{eff} = 4.94$, 4.76 B.M. is lower than predicted for five unpaired electrons. Anti-ferromagnetic exchange interaction between iron atoms in the crystal may account for this lower than spin-only value.

The electronic spectra are of little interpretive value with regard to gross structural features, Table II. All d–d transitions for high spin iron(III) are spin forbidden and are expected to be observed only weakly. The strong charge transfer bands which 'tail-off' into the visible mask these spin forbidden transitions. The relatively high extinction coefficient for each band maxima is too high to be attributed to a d–d transition alone. The lower energy band (ca. 20,000 cm^{-1}) is no doubt due to charge transfer between metal and ligand; whereas, the high energy band (ca. 30,000 cm^{-1}) may be an electronic transition localized on the ligand since the ligand spectra reveals absorption in this region.

TABLE II. Electronic Spectra (cm^{-1}).

Compound	Medium	Absorption Maxima[a]
Fe(SALDPT)Cl	Nujol	19,300; 32,300
	$CHCl_3$	19,084(1760); 30,770(7606)
	Pyridine	19,600(1990); 30,600(6760)
Fe(SALDIEN)Cl	Nujol	19,600; 33,300
	DMF	20,000(3930); 33,800(2880)
	Pyridine	19,900(2136); 22,400(1480); 31,200(7820)
Fe(SALDAES)Cl	Nujol	21,300; 29,410
	$CHCl_3$	18,980(2100); 30,770(9000)
	Pyridine	19,600(1742); 31,100(9560)

[a] Numbers in parentheses are molar extinction coefficients.

In conclusion, iron(III) complexes of three related pentadentate ligands have been prepared and characterized. The complexes are mononuclear in the solid state except for Fe(SALDAES)Cl which appears to possess appreciable iron–iron interaction as judged from its magnetic moment. A definite assignment of five or sic coordination cannot be made although infrared spectra indicates the latter for Fe(SALDPT)Cl. Coordination of the chloride ion in each case is inferred from the conductivity data in chloroform.

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