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Synthesis and Characterization of Cobalt(III) Complexes Derived from a Pentadentate Ligand Having Alkylamine and Thioether Donors to Enhance Stereospecificity

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Received March 21, 1978

The preparations and characterizations are described for the flexible, linear pentadentate ligand 7-methyl-4,10-dithia-1,7,13-triazatridecane (Q) and several monoacido cobalt(III) complexes of the type $Co(Q)X^{n+}$ ($X = Cl^-, Br^-, N_3^-, SCN^-, H_2O$). Having a flexible carbon chain between the donor atom sequence nitrogen–sulfur–nitrogen–sulfur–nitrogen generates the possibility for four distinct geometric isomers, designated $\alpha\alpha$, $\alpha\beta$, $\beta\beta$, and β-trans. Results suggest that the preferred pyramidal nature of sulfur and the methyl group positional requirements on the central nitrogen donor atom result in the select formation of the $\alpha\alpha$ geometry. Stereochemical considerations, visible electronic absorption spectra, and nuclear magnetic resonance spectra are discussed.

Introduction

It was initially our desire to design and synthesize flexible pentadentate ligands which would allow specific placement of thioether and/or nitrogen donor atoms trans to a single position in an octahedral geometry which could function as an electron-transfer site in oxidation–reduction reactions.[1-3] The multitude of geometric isomers common to pentadentate coordination affords the opportunity for both stereochemical variety and separation/identification dilemmas.[4-6]

To minimize the latter problem, our ligand design incorporated several features which we believed would stereochemically control the expected isomer distribution. Legg and Cook's researches using ethylenediamine-*N,N′*-diacetate and *N,N′*-dialkyl-substituted ethylenediamine-*N,N′*-diacetates demonstrated that placement of a methyl or ethyl group on the secondary nitrogen donor atoms of the quadridentate chelate limited the cobalt(III) geometric isomers to the α-cis configuration, whereas $Co(EDDA)(NH_3)_2^+$ was found to exist in α-cis and β-cis geometries.[7,8]

Searle, Petkovic, and Keene[9] examined the isomers which are formed by cobalt(III) when the ligand trien is modified by methyl substitution at the central nitrogen donor atoms. These workers synthesized complexes having the general formula $Co(4,7\text{-dimetrien})X_2^+$ (where 4,7-dimetrien = 4,7-dimethyl-1,4,7,10-tetraazadecane) and isolated both the α-cis and the β-cis isomers with the former being the predominant species. From thermodynamic considerations and the examination of scale molecular models they concluded the α-cis configuration is much more stable than the β-cis or the hypothetical trans isomers. The influence of thioether donor atoms in limiting cobalt(III) polydentate chelate isomer distributions was first demonstrated by Worrell and Busch[10] and later reaffirmed by Bosnich, Kneen, and Phillip.[11] The cobalt(III) complexes derived from $NH_2CH_2CH_2SCH_2CH_2SCH_2CH_2NH_2$ uniquely give only the α-cis geometry. Other configurations are possible when the ethylene chains are lengthened between adjacent donor atoms but the favored geometry remains α-cis > β-cis >>> trans.

Most stereoselective ligands make use of C=C or C=N double bonds and/or aromatic ring systems to constrain part or all of the ligand into a given arrangement. Our interest in oxidation–reduction processes precludes the incorporation of these groups into our design because they offer potential sites for attack by a reductant. The stereorestrictive nature of thioether and N-alkylated nitrogen donors appeared attractive for the design and synthesis of a new flexible, linear pentadentate,[12] $H_3CN(CH_2CH_2SCH_2CH_2NH_2)_2$. We report details for ligand synthesis and the preparation and physical characterization of several Co(III) complexes derived from Q.

Experimental Section

Visible absorption spectra were obtained using a Cary Model 14 recording spectrophotometer. Distilled water or 0.10 M perchloric acid was used as solvent. **Infrared specra** were obtained on a Perkin-Elmer Model 225 infrared spectrophotometer using Nujol or KBr pellet techniques. **Nuclear magnetic resonance spectra** were determined on a Varian Model A60 spectrometer. Complex spectra were determined in D_2O with 3-(trimethylsilyl)propanesulfonic acid as an internal reference.

Analyses. Cobalt analyses were performed on a Perkin-Elmer Model 103 atomic absorption system. All other microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

Ligand Synthesis

1,5-Dichloro-3-methyl-3-azapentane Hydrochloride. *Note: This compound is an extremely effective blister agent. Considerable caution is advised in this and the following reaction.* *N*-Methyl-2,2′-diethanolamine (200 g, 1.68 mol) dissolved in 400 mL of chloroform was placed in a 3-L round-bottom flask equipped with a stirrer, a 1-L dropping funnel, and a reflux condenser. Thionyl chloride (800 g, 6.71 mol) dissolved in 500 mL of chloroform was added slowly (4 h) with constant stirring. The pale yellow solution and white solid were refluxed, with constant stirring, for 4 h, and cooled to 25 °C.

Solid was collected by vacuum filtration and washed with several 25–50-mL portions of cold chloroform and ether. Filtrates were combined and reduced in volume on a rotary evaporator. The white solids were combined and dried in a vacuum desiccator equipped with a sodium hydroxide pellet trap; yield 270 g, 84%; mp 111–112 °C, lit.[13] mp 113–114 °C.

6-Methyl-3,9-dithia-2,10-diimino-1,6,11-triazaundecane Trihydrochloride. Thiourea (152 g, 1.99 mol) and crude 1,5-dichloro-3-methyl-3-azapentane hydrochloride (156 g, 1.00 mol) were refluxed for 3 h in 1 L of absolute ethanol. Dry hydrogen chloride gas was bubbled into the brown mixture with vigorous mechanical stirring. The cooled solid was collected by vacuum filtration and washed with cold ethanol and acetone and dried in a vacuum desiccator; yield 288 g, 84%; mp 203 °C (dec), lit.[14] mp 200 °C (dec).

4-Methyl-1,7-dithia-4-azaheptane. Warm, freshly prepared 10% sodium hydroxide (160 mL) was added to 6-methyl-3,9-dithia-2,10-diimino-1,6,11-triazaundecane trihydrochloride (97 g, 0.27 mol) dissolved in 200 mL of water in a 500-mL round-bottom flask. The brown mixture was heated to 95 °C with occasional agitation. A black, noxious oil separated to the top of the mixture. To prevent possible polymerization of the dithiol, a layer of benzene was poured on top of the cooling mixture to prevent air contact and, as an additional safeguard, the flask was filled with argon gas.

The cooled mixture was poured into a 500-mL separatory funnel and the dithiol extracted into four 100-mL portions of benzene. The benzene extracts were dried over sodium sulfate and then filtered, and the solvent was removed by rotary evaporation. The product isolated at this point was a light yellow oil (39.5 g). It was vacuum distilled at 11 torr and then argon-bled into the system to prevent polymerization. The distilled product was a clear, colorless oil with a pungent odor; yield 21.7 g, 53%; bp 104–106 °C (11 torr), lit.[14] bp 105–107 °C (11 torr).

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6-Methyl-3,9-dithia-6-aza-1,11-bis(*N*-phthalimido)undecane. Clean sodium metal (6.7 g, 0.29 mol) was dissolved in 400 mL of absolute ethanol under argon gas. The dithiol 4-methyl-1,7-dithia-4-azaheptane (21.7 g, 0.14 mol) was washed into the sodium ethoxide with absolute ethanol. The dithiolate was added slowly to a solution of *N*-(2-bromoethyl)phthalimide (72.9 g, 0.29 mol) dissolved in 500 mL of hot absolute ethanol. The mixture was refluxed for 0.5 h. Removal of the solvent by rotary evaporation left a viscous yellow oil mixed with a thick, white solid which was treated with 250 mL of distilled water. The aqueous phase was removed by decantation and discarded. This procedure was repeated three times. Acetone (300 mL) was added to the yellow oil/solid mixture. The mixture was warmed until the acetone acquired a deep yellow-gold color. Then the acetone portion was decanted and saved. This extraction was repeated with five additional 50-mL portions of acetone. A clean, white, coarse powder of unknown composition remained in the flask (mp >250 °C) and was discarded. Acetone was removed from the isolated supernatant by rotary evaporation leaving a thick, gold oil; yield 51.5 g, 73%.

7-Methyl-4-10-dithia-1,7-13-triazatridecane Trihydrochloride. 7-Methyl-3,9-dithia-7-aza-1,11-bis(*N*-phthalimido)undecane (51.5 g, 0.10 mol) was dissolved in 400 mL of refluxing ethanol. Excess hydrazine hydrate (20.5 g, 0.41 mol) dissolved in 20 mL of water was added slowly to the refluxing mixture (*caution! exothermic reaction*) and the solution refluxed for 0.5 h.

Concentrated hydrochloric acid (60 mL, 0.74 mol) was added to the mixture, and reflux was continued for 1.5 h with occasional agitation.

After the mixture was cooled, solid phthalhydrazide was removed by vacuum filtration and washed with several portions of distilled water (20 mL each), and washings were added to the filtrate. The filtrate volume was reduced on rotary evaporator until solvent was no longer removed at 90 °C. This product was used directly in the next step of the synthesis.

7-Methyl-4,10-dithia-1,7,13-triazatridecane. Solid NaOH (100 g) was added slowly to the above filtrate. During addition the reaction flask was maintained at 25 °C with an ice bath. A dark brown oil separated and was extracted into 2 L of ether in ~400-mL portions. The ethereal extract was dried over sodium sulfate and gravity filtered, and the ether was removed by rotary evaporation. The product was a viscous, yellow oil which was stored at −5 °C under argon; yield 22.5 g, 73%. The composition of Q is supported by elemental analyses for its Co(III) derivatives and its ^{1}H NMR spectrum which has a broad singlet at δ 1.86 which integrates for 4 H and is a normal chemical shift for a primary amine. A sharp singlet occurs at δ 2.34, integrates for 3 H, and is attributed to the methyl substituent on the tertiary amine. An intense multiplet between δ 2.50 and δ 3.20 is due to the protons on the four ethylene groups and integrates for 16 H.

Preparation of Cobalt(III) Complexes Derived from 7-Methyl-4,10-dithia-1,7,13-triazatridecane

Chloro(7-methyl-4,10-dithia-1,7,13-triazatridecane)cobalt(III) Tetrachlorocobaltate(II). Cobalt(II) chloride hexahydrate (5.5 g, 0.023 mol) dissolved in 60 mL of absolute methanol was aerated for 30 min with CO_2-free air, and then 7-methyl-4,10-dithia-1,7,13-triazatridecane (5.5 g, 0.023 mol) dissolved in 60 mL of absolute methanol was added slowly over 0.3 h and aeration continued for 3 h. Concentrated hydrochloric acid (7 mL) was added and the mixture placed in an ice bath. A deep blue powder was collected by vacuum filtration, washed with cold methanol and ether, and air-dried; yield 3.4 g, 28%. Anal. Calcd for $[Co(C_9H_{23}N_3S_2)Cl][CoCl_4]$: C, 20.30; H, 4.35. Found: C, 20.20; H, 4.19.

Chloro(7-methyl-4,10-dithia-1,7,13-triazatridecane)cobalt(III) Perchlorate. $[Co(Q)Cl][CoCl_4]$ (1.08 g, 0.020 mol) was dissolved in 25 mL of 0.5 M perchloric acid; the solution was warmed to 50 °C and filtered. Solid $NaClO_4$ (5 g) dissolved in 25 mL of 0.5 M $HClO_4$ was added slowly to the filtrate, and the filtrate was cooled at 5 °C overnight. Deep purple crystals were collected by vacuum filtration, washed with cold absolute ethanol and ether, and air-dried; yield 0.67 g, 62%. Anal. Calcd for $[Co(C_9H_{23}N_3S_2)Cl](ClO_4)_2$: C, 20.37; H, 4.36; N, 7.92; Co, 11.1. Found: C, 20.61; H, 4.38; N, 7.93; Co, 10.9.

Bromo(7-methyl-4,10-dithia-1,7,13-triazatridecane)cobalt(III) Tetrabromocobaltate(II). Cobalt(II) bromide hexahydrate (7.5 g, 0.023 mol) dissolved in 60 mL of absolute methanol was aerated for 0.3 h with CO_2-free air. 7-Methyl-4,10-dithia-1,7,13-triazatridecane (5.5 g, 0.023 mol), dissolved in 50 mL of absolute methanol, was added to the cobalt solution and air oxidation continued for 3 h before concentrated HBr (24 mL) was added. The green product was collected by vacuum filtration, washed with cold absolute ethanol, acetone, and ether, and air-dried; yield 3.8 g, 23%. Anal. Calcd for $[Co(C_9H_{23}N_3S_2)Br][CoBr_4]$: C, 14.32; H, 3.07. Found: C, 14.31; H, 2.98.

Bromo(7-methyl-4,10-dithia-1,7,13-triazatridecane)cobalt(III) Perchlorate. $[Co(Q)Br][CoBr_4]$ (0.98 g, 0.0013 mol) was dissolved in 30 mL of distilled water; the solution was filtered, and 20 mL of 1.0 M perchloric acid was added. The mixture was cooled, and green crystals were collected by vacuum filtration and washed exhaustively with cold absolute ethanol and ether and then air-dried; yield 0.65 g, 87%. Anal. Calcd for $[Co(C_9H_{23}N_3S_2)Br](ClO_4)_2$: C, 18.8; H, 4.04; N, 7.31; Co, 10.3. Found: C, 18.9; H, 4.20; N, 7.39; Co, 10.3.

Azido(7-methyl-4,10-dithia-1,7,13-triazatridecane)cobalt(III) Perchlorate. Solid NaN_3 (0.047 g, 0.72 mmol) was added to $[Co(Q)Cl](ClO_4)_2$ (0.25 g, 0.47 mmol) dissolved in 25 mL of distilled water at 40 °C. The color changed from purple to an intense blood red (0.3 h). Saturated aqueous $NaClO_4$ (4 mL) was added to the solution whereupon brown crystals formed which were collected by vacuum filtration, washed with cold absolute ethanol and ether, and air-dried; yield 0.24 g, 96%. Anal. Calcd for $[Co(C_9H_{23}N_3S_2)N_3](ClO_4)_2$: C, 20.1; H, 4.32; N, 15.6; Co, 11.0. Found: C, 20.0; H, 4.26; N, 15.6; Co, 10.9.

(Thiocyanato-*N*)(7-methyl-4,10-dithia-1,7,13-triazatridecane)cobalt(III) Perchlorate. This complex was prepared in a method analogous to that of $[Co(Q)N_3](ClO_4)_2$ except NH_4NCS replaced NaN_3. The red product was obtained in 64% yield and recrystallized from water. Anal. Calcd for $[Co(C_9H_{23}N_3S_2)NCS](ClO_4)_2 \cdot H_2O$: C, 21.0; H, 4.42; N, 9.82; Co, 10.3. Found: C, 20.8; H, 4.25; N, 9.74; Co, 10.4.

Nitro(7-methyl-4,10-dithia-1,7,13-triazatridecane)cobalt(III) Perchlorate. This orange complex was prepared in a manner analogous to that of $[Co(Q)N_3](ClO_4)_2$ except $NaNO_2$ replaced NaN_3. It was obtained in 60% yield. Anal. Calcd for $[Co(C_9H_{23}N_3S_2)NO_2](ClO_4)_2$: C, 19.7; H, 4.22; N, 11.7. Found: C, 19.7; H, 4.23; N, 11.6.

Results and Discussion

Ligand Synthesis. Several synthetic routes can be visualized for the preparation of 7-methyl-4,10-dithia-1,7,13-triazatridecane, Q. One usually good method for preparing thioethers is a reaction in which a thiol is condensed with a primary alkyl halide (i.e., 1 equiv of 1,5-dibromo-3-methyl-3-azapentane + 2 equiv of 2-mercaptoethylamine). Although the apparent simplicity of this reaction makes it an attractive synthetic route to Q, consideration of other systems utilizing similar reactions demonstrated otherwise.[10,15]

The most convenient route to Q involves the condensation of 1 equiv of 3-methyl-1,5-dithia-3-azapentane with 2 equiv of *N*-(2-bromoethyl)phthalimide. The resulting bis(*N*-phthalimido) compound can then be readily converted to ligand Q by hydrazinolysis with excess hydrazine hydrate.

3-Methyl-1,5-dimercapto-3-azapentane is not commercially available and was synthesized from *N*-methyl-2,2′-diethanolamine by conversion to 1,5-dichloro-3-methyl-3-azapentane hydrochloride by treatment with thionyl chloride. This mustard reacts with thiourea in boiling ethanol to give the hydrochloride salt of 6-methyl-3,9-dithia-2,10-diimino-1,6,11-triazaundecane. Base hydrolysis of the *S*-isothiourea yields the aminodithiol which can be purified by vacuum distillation. These compounds as their hydrochlorides are very hygroscopic. 1,5-Dichloro-3-methyl-3-azapentane is a dangerous nitrogen mustard, being a very effective and immediate blister agent. The distilled aminodithiol is a colorless liquid with an odor characteristic of thiols and must be handled under argon. On exposure to air, it undergoes rapid oxidation giving a viscous gum, presumably a chain-polymeric disulfide.

Stereochemical Considerations. Pentadentate coordination generates four geometrical isomers designated $\alpha\alpha$, $\alpha\beta$, $\beta\beta$, and β-trans (Figure 1).[16]

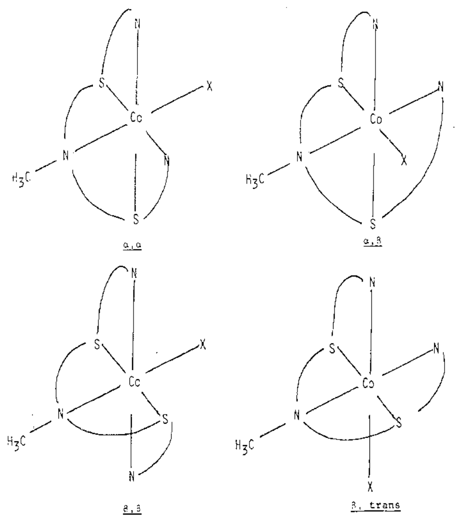

Figure 1. Geometrical isomers for $Co(Q)X^{2+}$ ions.

In the case of $Co(Q)X^{n+}$, three of the possible four geometric isomers (αβ, ββ, β-trans) exist as nonsuperimposable mirror images, generating a possible total of six optical isomers. Two thioether and one *N*-alkyl nitrogen donor can each assume *R* or *S* arrangements. Each geometric isomer possesses four chelate rings that can form, in concert, 17 distinct ring conformation combinations. These features serve to illustrate the formidable task of separating and identifying the isomers that can be generated by pentadentate coordination.

Steric requirements of the *N*-methyl substituent coupled with the strictly tetrahedral bonding disposition around nitrogen minimize bond angle strain within adjacent chelate rings. This feature coupled with the bond angle requirements of thioether donors is expected to greatly reduce or eliminate the production of isomers in which two or more donor atoms and adjacent ring systems occupy in-plane orientations (β or trans).[10,11] These factors and the results of the stereochemical studies cited in the Introduction suggest that the dominant metal isomer configuration with Q would possess the αα topology.

Characterization of Cobalt(III) Complexes. The normal chemical interconversions of $Co(Q)L^{n+}$ complexes are summarized in Figure 2. They are very soluble complexes as halide salts but can be isolated initially as $ZnCl_4^{2-}$ or CoX_4^{2-} salts which are then reprecipitated as the less soluble ClO_4^- salts. They exhibit molar conductances in the range 188–215 Ω^{-1} cm^2 mol^{-1} which is consistent with their formulation (1:2 electrolyte) as deduced from elemental analyses. Numerous chemical interconversions consistently gave the same geometrical isomer as evidenced by careful examination of IR and UV–visible spectra. Attempts to observe and identify more than one geometric form failed. $Co(Q)Cl^{2+}$ and $Co(Q)Br^{2+}$ aquate slowly whereas $Co(Q)NO_2^{2+}$ is stable toward aquation. Chromatography (paper and TLC) using the latter compound support the isolation of only one species. The complexes tend to be immovable on cation-exchange resin. Separation into optical isomers using either 1:1 or 1:2 molar ratios of complex ($Co(Q)NO_2^{2+}$, $Co(Q)Cl^{2+}$) to resolving agent (*d*-tartaric acid, SbO-*d*-tart, (−)-$Co(ox)_2en^-$) failed to give diastereoisomer formation. Although not definitive proof of the αα geometry, the results of these experiments strongly favor it.

Table I. Electronic Spectra for $Co(Q)X^{2+}$ Complexes

compd	λ_{max}, nm (ε, M^{-1} cm^{-1})^a
$Co(Q)Br^{2+}$	586 (242), 505 (148),^{b} 350 (1145), 281 (21 950)
$Co(Q)Cl^{2+}$	565 (207), 505 (159),^{b} 386 (235), 278 (15 260)
$Co(Q)N_3^{2+}$	547 (725), 335 (6356)
$Co(Q)NCS^{2+}$	534 (580), 355 (1820), 284 (14 050)
$Co(Q)H_2O^{3+}$	518 (186), 380 (183),^{b} 290 (15 610)
$Co(Q)NO_2^{2+}$	490 (318), 346 (568)

^{a} ClO_4^- salts dissolved in H_2O at 20 °C. ^{b} Shoulder.

The ^{1}H NMR spectrum of $Co(Q)Cl^{2+}$ exhibits a sharp singlet at δ 2.38 attributed to the *N*-methyl group. The observed chemical shift is within the range (δ 2.1–3.0) normally observed for a methyl group attached to a nitrogen. Searle, Petkovic, and Keene[9] observed a chemical shift of δ 2.43 for the *N*-methyl groups in α-*cis*-[Co(dimetrien)Cl$_2$]$^+$. Legg and Cooke[7] reported that the methyl component in α-*cis*-[Co(DMEDDA)(en)]$^+$ resonates at δ 2.67. It is expected that, if the isolated $Co(Q)Cl^{2+}$ complex were a mixture of isomers, the methyl substituent in the different geometries would be influenced by different environments (accidental coincidence is possible but unlikely). The manifestation of this would be more than one methyl resonance as illustrated by the ^{1}H NMR spectra of α-*cis*- and β-*cis*-[Co(dimetrien)Cl$_2$]$^+$.[9] The chemical shift of the α-cis complex, in which both methyl groups are equivalent, is a sharp singlet δ 2.43. In contrast, the β-cis isomer exhibits methyl resonances at δ 2.32 and 2.78 due to stereochemically nonequivalent methyl groups. Because of the explicitly single methyl resonance for $Co(Q)Cl^{2+}$, we conclude that the isolated complex is not a mixture but a pure geometric isomer.

The wavelength of maximum absorption and related absorption coefficients are compiled in Table I. Both $Co(Q)Cl^{2+}$ and $Co(Q)Br^{2+}$ exhibit distinct splitting of the lowest energy d–d envelope. The other complexes exhibit a single sym-

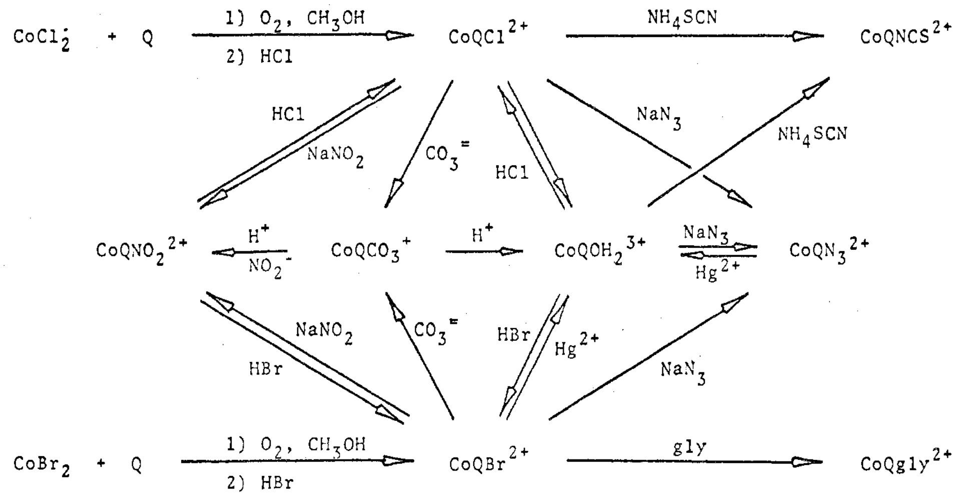

Figure 2. Chemical interconversions for several $Co(Q)L^{n+}$ complexes.

metrical absorption shifted to higher energy followed by an intense charge-transfer band in the near-UV region. The ϵ values are significantly higher than corresponding pentaamine complexes, demonstrating the dramatic influence coordinated thioether groups have on electronic spectra. The energy of the low-energy absorption band for these complexes is consistent with the normal spectrochemical series $Br^- < Cl^- < N_3^- < SCN^- < H_2O \ll NO_2^-$. Also, it demonstrates that the nitrogen atom in SCN^- and NO_2^- is coordinated.

As in similar stereochemical studies,[8-10] infrared spectra were found to be inconclusive in assigning the topological donor configuration for these complexes. In general, the N–H stretching region (3000–3400 cm^{-1}) exhibited three to five strong absorptions and a single strong N–H deformation band at $\sim$1575 cm^{-1}. $[Co(Q)NO_2](ClO_4)_2$ exhibited characteristic nitro (NO_2)[17] absorptions at 620, 825, 1320, and 1430 cm^{-1}. Terminal Co–NCS binding is supported by the C=N stretch at 2110 cm^{-1} for $[Co(Q)NSC](ClO_4)_2$.[18]

The synthesis and characterization of a new pentadentate ligand containing three nitrogen and two sulfur donors are reported. It coordinates to Co(III) giving a series of complexes $Co(Q)X^{n+}$, which we believe to possess the same $\alpha\alpha$ topology. This is a result of ligand design and stereochemical bonding angle requirements of both $CH_3N<$ and –S– donor atoms.

Registry No. $[Co(Q)Cl][CoCl_4]$, 67904-86-3; $[Co(Q)Cl](ClO_4)_2$, 67904-87-4; $[Co(Q)Br][CoCl_4]$, 64659-36-5; $[Co(Q)Br](ClO_4)_2$, 64659-37-6; $[Co(Q)N_3](ClO_4)_2$, 67904-89-6; $[Co(Q)NCS](ClO_4)_2$, 67904-91-0; $[Co(Q)NO_2](ClO_4)_2$, 67904-93-2; $Co(Q)H_2O^{3+}$, 67904-94-3; 1,5-dichloro-3-methyl-3-azapentane hydrochloride, 17027-23-5; 6-methyl-3,9-dithia-2,10-diimino-1,6,11-triazaundecane trihydrochloride, 63915-53-7; 4-methyl-1,7-dithia-4-azaheptane, 19031-92-6; 6-methyl-3,9-dithia-6-aza-1,11-bis(*N*-phthalimido)undecane, 67891-61-6; Q, 62121-70-4; *N*-methyl-2,2′-diethanolamine, 105-59-9; thionyl chloride, 7719-09-7; thiourea, 62-56-6; *N*-(2-bromoethyl)phthalimide, 574-98-1.

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(16) Nomenclature is extended from the α,β nomenclature Sargeson and Searle used for trien complexes.[8] The coordinated Q ligand, viewed from the two ends, has either α,β or trans characteristics when the arrangement of the first four donor atoms is considered. The $\alpha\alpha$ structure has a donor arrangement like that of α-*cis*-$[Co(trien)X_2]^{n+}$ when viewed from either end. The $\alpha\beta$ structure has α and β configurations. Similarly the isomers denoted $\beta\beta$ and β-trans reflect both the β and/or trans configurations when viewed from both ends of the chelate chain.
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Nitrosylbis(diorganodithiocarbamato)iron Complexes. Effect of Organic Substituents

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Received March 24, 1978

A series of 14 $Fe(NO)(S_2CNRR')_2$ complexes have been prepared, where R and R′ are either aliphatic or aromatic organic substituents. Room-temperature Mössbauer, infrared, and EPR measurements are included in this report. The N–O stretching frequency (both in chloroform solution and in Nujol) exhibits a nearly linear dependence on the "corrected" aqueous pK_a (pK_a(cor)) values of $H_2NRR'^+$, which confirms that the resonance effects which diminish the basicity of the nitrogen lone pair of electrons in HNRR′ in solution are absent in the aromatic dithiocarbamates. The change in each spectroscopic parameter, infrared NO stretching frequency, ^{57}Fe Mössbauer isomer shift and quadrupole splitting, and EPR g_{eff} value and ^{14}N hyperfine splitting with pK_a(cor) is explained on the basis of a single model which includes the inductive effects of R and R′, iron–nitrosyl back-bonding, and the occupation of the Fe d_{z^2} orbital by the unpaired electron.

Introduction

The nitrosylbis(diorganodithiocarbamato)iron complexes ($FeNO(dtc)_2$, where dtc is $S_2CNRR'^-$ and R and R′ are organic substituents) are a series of compounds in which several spectroscopic techniques can probe the effect of varying R and R′ on the ligand field strength of $^-S_2CNRR'$. Only a few of these derivatives (usually R,R′ = Me or R,R′ = Et) have been investigated by IR,[1,2,5] EPR,[2-6] UV–vis,[5] and Mössbauer[1,7] techniques, even though they were first synthesized in 1931.[8] Recently, Ileperuma and Feltham[9] reported the preparation, IR spectra, and reactions of four derivatives (R,R′ = Me; Et; Ph; R = Me, R′ = Ph). These results combined with X-ray structure determinations[10-12] yield the picture of a square-pyramidal complex with the NO bond axis perpendicular to the plane of the four sulfurs. The similarity of the trends of N–O stretching frequencies in $CHCl_3$ solution and Nujol mulls reported below supports our expectation that the square-pyramidal configuration is maintained. These complexes, however, are probably not sterically rigid in solution; indeed, the corresponding $Fe(dtc)_3$ complexes exhibit two distinct kinetic processes, a trigonal twist and a cis–trans isomerization, in CH_2Cl_2 at −20 °C and below.[13] The unpaired electron in these spin = $^1/_2$ compounds has been presumed to occupy an a_1 (d_{z^2}) molecular orbital.[9]

Little attention has been paid to the effect of changing organic substituents (R,R′) on the dithiocarbamate ligand in this set of complexes. In the corresponding iron(III) series, $Fe(dtc)_3$, changing the organic substituents causes a change in the magnetic moments[14] and, hence, a set of spin-crossover

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