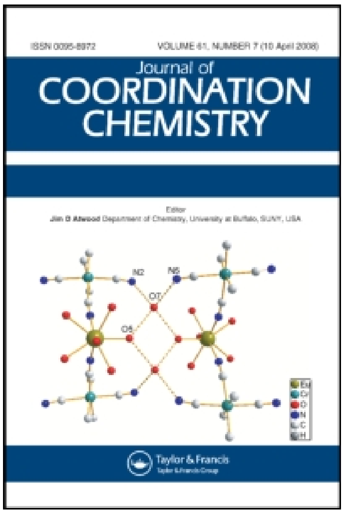

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PREPARATION, ISOLATION, AND CHARACTERIZATION OF COBALT (III) COMPLEXES DERIVED FROM A NEW LINEAR, FLEXIBLE PENTADENTATE LIGAND 1, 11-DIAMINO-3, 6, 9-TRITHIAUNDECANE

J. H. Worrell[a]; P. Behnken[a]; R. A. Goddard[a]
[a] Department of Chemistry, University of South Florida, Tampa, Florida

To cite this Article Worrell, J. H. , Behnken, P. and Goddard, R. A.(1979) 'PREPARATION, ISOLATION, AND CHARACTERIZATION OF COBALT (III) COMPLEXES DERIVED FROM A NEW LINEAR, FLEXIBLE PENTADENTATE LIGAND 1, 11-DIAMINO-3, 6, 9-TRITHIAUNDECANE', Journal of Coordination Chemistry, 9: 1, 53 — 58

To link to this Article: DOI: 10.1080/00958977908073101

URL: http://dx.doi.org/10.1080/00958977908073101

J. Coord. Chem.
1979, Vol. 9, pp. 53–58

PREPARATION, ISOLATION, AND CHARACTERIZATION OF COBALT(III) COMPLEXES DERIVED FROM A NEW LINEAR, FLEXIBLE PENTADENTATE LIGAND 1, 11-DIAMINO-3, 6, 9-TRITHIAUNDECANE

J. H. WORRELL,† P. BEHNKEN and R. A. GODDARD

Contribution from the Department of Chemistry, University of South Florida, Tampa, Florida 33620

(Received May 24, 1978; in final form September 4, 1978)

The reaction of bis(2-mercaptoethyl)sulfide with N-(β-bromoethyl)phthalimide followed by hydrolysis using hydrazine hydrate afforded 1,11-diamino-3,6,9-trithiaundecane, $NH_2CH_2CH_2-S-CH_2CH_2-S-CH_2CH_2-S-CH_2$-$CH_2NH_2$, (QS). The preparations and interconversions of Cobalt(III) complexes of the type $Co(QS)X^{n+}$ where $X = Cl^-, Br^-, N_3^-, NO_2^-$ and SCN^- are presented and discussed. Considerations are presented supporting the αα geometry for this series of complexes.

INTRODUCTION

The present work describes the synthesis and properties of octahedral cobalt(III) complexes derived from a new flexible, linear sulfur containing pentadentate ligand, 1,11-diamino-3,6,9-trithiaundecane[1] which coordinates via two terminal $-NH_2$ groups and three thioether, R–S–R, donor centers. $H_2N-CH_2CH_2-S-CH_2CH_2-S-CH_2CH_2-S-CH_2CH_2-NH_2$. Its all nitrogen analog is tetraethylene-pentamine.[2] The selective placement of three thioether linkages in the present ligand will affort the opportunity to examine the influence of sulfur donors on metal complex electronic spectra, rates of substitution[3] and electron transfer[4] reactions, and ligand stereospecificity.[5,6] Bond angle requirements around the coordinated sulfur atoms suggest that the usual geometric isomer distribution expected for pentadentate coordination would be limited in the present case.[5]

EXPERIMENTAL

Analyses and Physical Measurement

Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. Infrared spectra were obtained by mull techniques using KBr discs and a Beckman Acculab 3 instrument. Electronic absorption spectra were obtained in aqueous solution using a Cary 14 recording spectrophotometer with quartz cells. Conductivity measurements were performed in aqueous solution with platinum electrodes (complex, 10^{-3}–10^{-4} *M*) using a Sefass model RCM 15B2 conductivity bridge manufactured by Beckman Instruments.

Preparation of 1,11-Diamino-3,6,9-Trithiaundecane

Bis(2-mercaptoethyl)sulfide obtained from Aldrich Chemical Company was used without further purification. Sodium metal was acquired from Fisher Scientific Company and N-(β-bromoethyl)phthalimide from Eastman Organic Chemicals. Hydrazine hydrate (99%) was obtained from Matheson, Coleman and Bell. All other reagents and solvents were obtained from commercial sources and used as received.

Sodium metal (9.44 g, 0.41 mol) was cut, and cleaned by alternate immersion in absolute C_2H_5OH and ether, weighed, and added to a 3 litre, 3-neck round bottom flask containing 300 ml of absolute C_2H_5OH. The reaction is exothermic and caution is exercised so as to avoid a rapid boil-off of C_2H_5OH and H_2. When the Na was dissolved (∿2 hrs), bis-(2-mercaptoethyl)sulfide (30.9 g, 0.20 mol) was added slowly with stirring. This mixture was refluxed for several minutes. A hot solution of N-(β-bromoethyl)phthalimide (123.2 g, 0.49 mol) dissolved in 625 ml of absolute C_2H_5OH was added slowly with stirring to the dithiolate solution. Refluxing was continued for 1.5 hrs. On cooling the product was collected by suction filtration and washed with water. The damp suction dried yield of 1,11-bis-(phthalimide)-3,6,9-trithiaundecane was 112 g. A portion of this product was recrystallized from boiling acetone to give a white solid, melting point 95.5–96.3°C. Anal. Calcd. for $C_{24}H_{28}N_2O_4S_3$: C, 61.3; H, 4.37; N, 5.10. Found: C, 61.8; H, 4.52; N, 4.95.

1,11-bis(phthalimide)-3,6,9-trithiaundecane (101.9 g, 0.20 mol) was dissolved in 2250 ml of absolute C_2H_5OH in a 3-neck, 3 litre round bottom flask. A reflux condenser was attached and the mixture heated to dissolve the solid. Hydrazine hydrate (99%, 30.5 ml, 0.63 mol) in 30 ml distilled H_2O, was added slowly. The yellow solution was refluxed for 1.25 hrs. Concentrated HCl (38%, 12.4 *M*, 100 ml, 1.2 mol) was then added slowly to the cream colored mixture. Reflux was continued for an additional 1.5 hr, the mixture was cooled overnight at 5°C. The white precipitate of phthalhydrazide was separated by suction filtration and washed carefully with four 25 ml portions of distilled H_2O. Both filtrate and washings were combined and their volume reduced on a rotary evaporator to $\sim$200 ml.

The 1,11-diamino-3,6,9-trithiaundecane dihydrochloride solution was transferred to a 2-litre erlenmeyer flask containing 500 ml of diethylether. Solid NaOH (250 g, 6.3 mol) was added slowly with stirring. An ice bath was employed to control the exothermic neutralization of HCl. The ether layer was carefully collected and fresh anhydrous ether added to the mixture. A total of 1.5 litres of ether-ligand extract was collected, dried over NaOH, filtered, and then the ether removed by rotary evaporation to yield 16.0 g (35%) of white waxy solid. Ligand QS was used directly for metal complex syntheses and the elemental analyses for the complexes confirms an empirical formula of $C_8H_{20}N_2S_3$.

α,α-(1,11-Diamino-3,6,9-trithiaundecane)chlorocobalt(III) perchlorate Co(II) chloride hexahydrate (20.6 g, 87 mmol) dissolved in 250 ml CH_3OH was aerated for 20 min. 1,11-Diamino-3,6,9-trithiaundecane (13.9 g, 58 mmol) dissolved in 280 ml CH_3OH was added to the Co(II) solution dropwise over a period of one hr. After addition of the ligand, two drops of conc. HCl was added and the solution stirred and aerated an additional 30 min. Additional conc. HCl (50.0 ml, 0.60 mol) was added dropwise, aeration stopped and the mixture heated for 20 min. Overnight cooling followed by filtration gave a blue solid which was washed with 5 ml portions of cold absolute C_2H_5OH and ether and air dried. The salt isolated is [Co(QS)Cl] [$CoCl_4$]$^{\cdot 7}$; yield 19% (6.0 g, 11.2 mmol).

To prepare the ClO_4^- salt, (1,11-diamino-3,6,9-trithiaundecane)chlorocobalt(III) tetrachlorocobaltate(II) (4.6 g, 8.6 mmol) was dissolved in 40 ml of distilled H_2O, filtered and 5 ml of aqueous saturated $NaClO_4$ added. The solution was cooled, filtered, and the purple crystalline product washed with 5 ml portions of cold absolute C_2H_5OH and ether and air dried. The product was collected in 80% yield (3.7 g, 6.9 mmol).

It was recrystallized by dissolution in 80 ml distilled water, followed by filtration, and addition of aqueous $NaClO_4$ solution (20 g in 10 ml). A qualitative test for Co^{2+} proved negative, indicative of complete conversion of the tetrachlorocobaltate(II) salt to the perchlorate salt. Anal. Calcd. for $C_8H_{20}Cl_3CoN_2O_8S_3$, [Co(QS)Cl]$(ClO_4)_2$: C, 18.0; H, 3.78; N, 5.25; S, 18.0. Found: C, 17.9; H, 3.62; N, 5.20; S, 17.4.

α,α-(1,11-Diamino-3,6,9-trithiaundecane)bromocobalt(III) perchlorate Co(II) bromide hexahydrate (6.8 g, 21 mmol) dissolved in 50 ml of CH_3OH is stirred and aerated for 20 min. 1,11-Diamino-3,6,9-trithiaundecane (5.0 g, 21 mmol) dissolved in 50 ml of CH_3OH is added dropwise to the Co(II) solution over a period of 30 min. The suspension was stirred and aerated for one hr, then concentrated HBr (10.0 ml, 9 mmol) added dropwise. Stirring and aeration was continued for an additional 1.5 hrs. and the mixture again boiled for 30 min, accompanied by the dropwise addition of 5.0 ml of concentrated HBr (45 mmol) whereupon the color of the precipitate changes from brown to dark green. The mixture was cooled and the green product collected by filtration, washed successively with cold absolute C_2H_5OH and ether and air dried. The product obtained was [Co(QS)Br] [$CoBr_4$];[7] yield 19% (2.95 g, 3,89 mmol).

To convert the complex to the perchlorate salt, [Co(QS)Br] [$CoBr_4$] (2.5 g, 2.84 mmol) is dissolved in 60 ml of distilled H_2O. This purple solution is filtered, 10 g of $NaClO_4 \cdot H_2O$ is added as a solid, and the mixture stored at 5°C for one hr. A bluish-purple powder is collected and washed with 5 ml portions of cold absolute C_2H_5OH and ether and air dried. The qualitative test for Co^{2+} proved negative. A 94% yield (1.54 g, 2.66 mmol) was obtained in the conversion. Anal. Calcd. for $C_8H_{20}BrCl_2CoN_2O_8S_3$,

$[Co(QS)Br](ClO_4)_2$: C, 16.6; H, 3.49; N, 4.84. Found: C, 16.8; H, 3.76; N, 4.92.

α,α-(1,11-Diamino-3,6,9-trithiaundecane)azidocobalt(III) perchlorate (1,11-Diamino-3,6,9-trithiaundecane)chlorocobalt(III) perchlorate (0.5 g, 0.9 mmol) was dissolved in 60 ml of distilled H_2O. Sodium azide (0.2 g, 3.1 mmol) was added and the solution stirred for 50 min. Solid $NaClO_4 \cdot H_2O$ is added followed by $HClO_4$ (4 ml 2 *M*) and the solution stored at 5°C for 40 min. The solid was collected by vacuum filtration, washed with cold absolute C_2H_5OH and ether and air dried. The dark purple plates are recrystallized by dissolving in a minimum volume of distilled H_2O (30 ml) and adding 4 ml of 2 *M* $HClO_4$. An immediate precipitate forms, which is collected by filtration, washed with cold absolute C_2H_5OH and ether and air dried. Yield 70% (.34 g, 0.63 mmol). Anal. Calcd. for $C_8H_{20}Cl_2CoN_5O_8S_3$, $[Co(QS)N_3](ClO_4)_2$: C, 17.8; H, 3.73; N, 12.9. Found: C, 17.9; H, 3.88; N, 12.7.

α,α-(1,11-Diamino-3,6,9-trithiaundecane)nitrocobalt(III) perchlorate α,α-$Co(QS)NO_2^{2+}$ may be prepared from either $[Co(QS)Br](ClO_4)_2$ or $[Co(QS)Cl](ClO_4)_2$ by treatment with $NaNO_2$ in aqueous media. In a typical preparation, $[Co(QS)](ClO_4)_2$ (0.44 g, 0.83 mmol) was dissolved in a minimum volume of H_2O to which $NaNO_2$ (0.46 g, 6.6 mmol) was added with stirring and warming to ∿40°C. Upon standing for 1 hr the color changes from purple to red-orange. The $[Co(QS)NO_2](ClO_4)_2$ was precipitated by the addition of $HClO_4$ and collected by filtration. Recrystallization from water with dilute $HClO_4$ gives 87% yield (0.39 g, 0.72 mmol) of pure $[Co(QS)NO_2](ClO_4)_2$. Anal. Calcd. for $C_8H_{20}Cl_2CoN_3O_{10}S_3$, $[Co(QS)NO_2](ClO_4)_2$: C, 17.6; H, 3.70; N, 7.72. Found: C, 17.5; H, 3.41; N, 7.57.

α,α-(1,11-Diamino-3,6,9-trithiaundecane)thiocyanatocobalt(III) perchlorate Treatment of $[Co(QS)Cl](ClO_4)_2$ (0.127 g, 0.24 mmol), dissolved in a minimum volume of H_2O, with NaNCS (0.065 g, 0.80 mmol) results in the formation of a red solution. Addition of 2 ml of saturated aqueous $NaClO_4$ solution causes precipitation of $[Co(QS)NCS](ClO_4)_2$. Recrystallization and isolation from warm H_2O gives a red crystalline solid in 80% yield (0.10 g, 0.18 mmol). Anal. Calcd. for $C_9H_{20}Cl_2CoN_3O_8S_4$, $[Co(QS)NCS](ClO_4)_2$: C, 19.4; H, 3.62; N, 7.55. Found: C, 19.2; H, 3.47; N, 7.36.

RESULTS AND DISCUSSION

The new ligand described in this work can be considered as the sulfur analogue of tetraethylenepentamine, (tetren).[2] It is a flexible, linear pentadentate having a donor atom sequence Nitrogen–Sulfur–Sulfur–Sulfur–Nitrogen. It may be visualized as a tetren ligand in which the three inner secondary nitrogen atoms have been replaced by thioether donor atoms. The synthesis of 1,11-diamino-3,6,9-trithiaundecane,[1] (QS), begins by treatment of bis(2-mercaptoethyl)-sulfide in sodium ethoxide with two equivalents of N-(β-bromoethyl)phthalimide to produce a water insoluble product 1,11-bis(phthalimide-3,6,9-trithiaundecane having a melting point of 96°C. The NaBr formed in the reaction is removed by washing the product with distilled water. The phthalimide groups are removed by hydrolysis using hydrazine hydrate and concentrated hydrochloric acid. The resultant water soluble 1,11-diamino-3,6,9-trithiaundecane dihydrochloride is separated from the water insoluble phthalhydrazide by suction filtration. The dihydrochloride ligand salt need not be isolated as a solid. Concentration of the aqueous solution followed by neutralization using sodium hydroxide allows the free diamine to be extracted into anhydrous ether. Removal of ether by evaporation produces a solid white waxy material, ligand QS, which can be used directly in the preparation of metal complexes.

The reaction sequence employs methodology suitable for the preparation of a wide variety of new ligands simply by changing the structural nature of the dithiol or amine moiety.

Stereochemical Considerations

As in the case of tetraethylenepentamine,[2,8] four distinct geometric isomers, designated αα, ββ, αβ, and βtrans are possible. These are shown in Figure 1. The isomer designations are an extension of the α, β, and trans nomenclature used for triethylenetetramine complexes.[9,10] Beginning at each terminal $-NH_2$ donor atom of coordinated QS and moving along the chelate ring system, one arrives at an α, β, or trans designation depending upon the positions of three consecutive chelate rings.[11] The αα geometry has a donor atom and chelate ring arrangement like that of α-*cis*-$Co(trien)X_2^{n+}$ when viewed from both terminal $-NH_2$'s.

The αβ, ββ, and βtrans geometries each should exist in racemic optical pairs, whereas the αα configuration possesses a plane of symmetry thus precluding its existence as potentially resolvable.

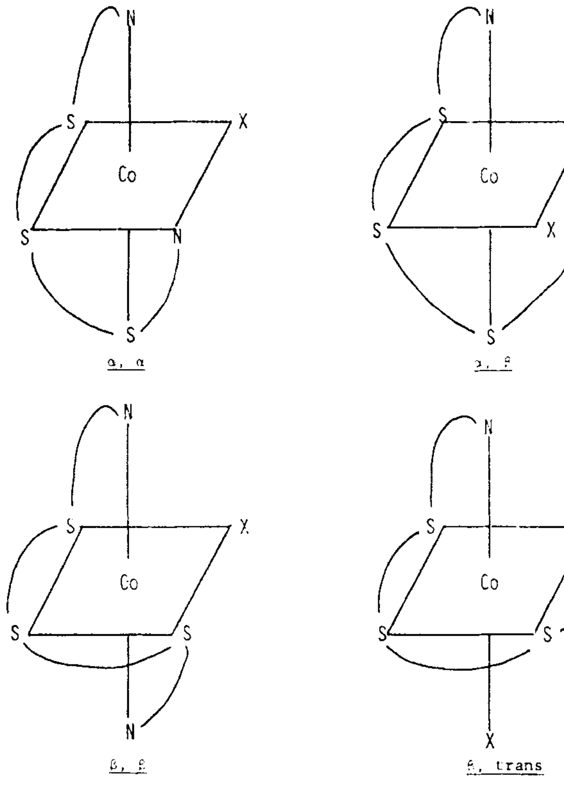

FIGURE 1 Geometric isomers of $Co(QS)X^{2+}$ ions.

Molecular models of $Co(QS)X^{n+}$ favor the αα form in terms of donor-atom ring-strain considerations, that is, the most bond angular strain occurs at the thioethers where the ligand is turning from one chelate ring to the next. This strain is minimized in the αα configuration.

Previous experimental studies have demonstrated that when successive sulfur donor atoms are separated by a two-carbon chain ($-CH_2CH_2-$) only the α configuration is observed.[5,6] Only chain lengthening between thioether donors can facilitate the production of the β arrangement.[12,13] The *trans* geometry, although favorable in all-nitrogen donor quadridentates, is least favored in ligands derived from thioether donors.[12]

In the present work we would anticipate the dominant isolatable isomer to be in the αα form, followed by αβ, then ββ. The severe strain present in the βtrans isomer makes its existence highly unlikely.

Synthetic Studies

A very general route to the cobalt(III) complexes of 1,11-diamino-3,6,9-trithiaundecane involves the air oxidation of an appropriate cobalt(II) salt and the ligand hydrohalide in methanol and/or methanol-water mixtures. Octahedral complexes of the general type $Co(QS)X^{2+}$ where the monodentate X is Cl^-, Br^-, NO_2^-, SCN^-, N_3^-, etc., can be prepared by aqueous metathetical interaction of $Co(QS)Cl^{2+}$ with the appropriate NaX salt or HX acid. Often one can most readily isolate the complex as the $ZnCl_4^{2-}$ or the CoX_4^{2-} salt then upon dissolution in warm water, recrystallize it as the perchlorate salt by the addition of aqueous $HClO_4$–$NaClO_4$. Analytical data for carbon hydrogen, nitrogen and in some cases sulfur, have been obtained and support the proposed stoichiometries of these new compounds. A number of interconversions are summarized in Figure 2.

The expected presence of more than one geometrical isomer of $Co(QS)X^{2+}$ prompted the careful examination of electronic and vibrational spectra in conjunction with numerous interconversion reaction products. Fractional crystallization and examination of IR and visible spectra for each fraction did not provide evidence for multiple geometric isomers. The products isolated were interconverted, i.e., $Cl \rightarrow NO_2 \rightarrow Br \rightarrow N_3$ and the infrared and visible spectra of the resultant compounds were found to be identical to the spectrum obtained for a given compound when it was prepared by an independent synthetic route directly from a cobalt(II) salt in the presence of appropriate ligands. Chromatography (TCC and paper) using $Co(QS)NCS^{2+}$ and $Co(QS)NO_2^{2+}$ failed to demonstrate the presence of more than a single species in each case. This suggests the absence of several geometrical isomers in the isolated solids.

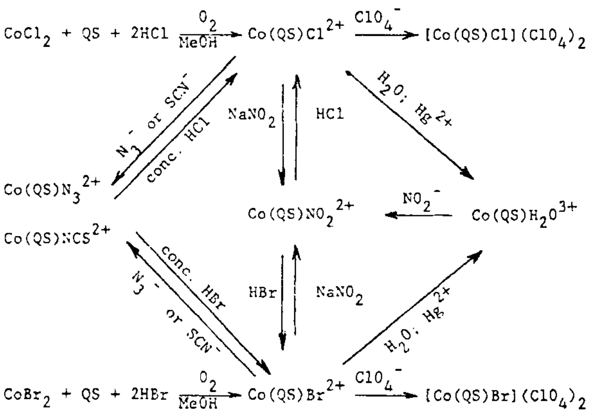

FIGURE 2 Chemical interconversions for $\alpha,\alpha,Co(QS)L^{2+}$ complexes.

Molar Conductance

The molar conductance of each of the complexes is 215 ± 10 ohm^{-1}cm^2. This is normal for a diunivalent electrolyte, hence the conductivity data, together with the elemental analyses given in the experimental section corroborate the formulation $[Co(QS)X](ClO_4)_2$ for these complexes.

Electronic Absorption Spectra

The wavelengths of maximum absorption relative to each complex are compiled in Table I along with their corresponding absorption coefficients. In the case of $Co(QS)Cl^{2+}$ and $Co(QS)Br^{2+}$ a shoulder absorption lies on the low energy side of a UV charge transfer band, demonstrating that compounds of this new family have the typical two envelope absorption spectrum characteristic of most cobalt(III) complexes. The remaining complexes, $Co(QS)N_3{}^{2+}$, $Co(QS)NCS^{2+}$, and $Co(QS)NO_2{}^{2+}$ exhibit a single symmetrical absorption envelope in the visible region. It is especially noteworthy that the absorption coefficients for the lowest energy d–d envelopes are 3 to 10 times the values observed for similar complexes derived from ammine or pentadentate ligands containing nitrogen donors.[2] The observed spectrochemical series follows the order $Br^- < Cl^- < N_3{}^- < NCS^- < NO_2{}^-$, supporting the assignment that the nitrogen atom of $-NCS^-$ and $-NO_2{}^-$ are coordinated.

Infrared Spectral Characteristics

As has been found to be the case in other stereochemical studies,[2,5,10,12] the number and pattern of N–H stretching bands (∿3000–3400 cm^{-1}) and/or NH_2 deformation bands (∿1600 cm^{-1}) do not provide definitive geometric isomer assignments. In general 3–4 distinct, strong absorptions are observed for this series of compounds in the range 3000–3400 cm^{-1} in conjunction with a single strong absorption at ∿1600 cm^{-1}. Dominant ligand and/or perchlorate anion absorptions in all the above complexes are observed at ∿1145, 1080, 1050, 1020, 1005, 995 and 930 cm^{-1}. That the complexes, $[Co(QS)X](ClO_4)_2$, where X = Cl^-, Br^-, SCN^-, $N_3{}^-$ and $NO_2{}^-$ all possess a common geometrical configuration is supported by the exceptional number of identical ligand IR absorption bands observed for all five complexes. IR bands[14] at 1435 and 1315 cm^{-1} support nitro ($-NO_2$) coordination in $[Co(QS)NO_2](ClO_4)_2$. The intense absorption at 2050 cm^{-1} suggests M–N azide coordination in $[Co(QS)N_3](ClO_4)_2$. The $[Co(QS)NCS](ClO_4)_2$ C≡N stretch at 2110 cm^{-1} is consistent with a terminal M–NCS binding arrangement.[15]

Optical Isomers

A number of careful resolution experiments using d-tartaric acid, antimonyl-d-tartrate and (+) $Na[Co(en)(ox)_2]$ have failed to yield a separation of optical isomers for $Co(QS)Cl^{2+}$ and $Co(QS)NO_2{}^{2+}$. This experimental evidence is consistent with the αα configurational assignment but not definitive proof of it.

CONCLUSIONS

A new pentadentate (NSSSN) ligand, and a series of cobalt(III) complexes were synthesized and characterized by elemental analyses, conductance, electronic spectra, and infrared spectra. Although four geometrical isomers are theoretically possible for this metal–ligand combination, available experimental evidence suggests only one geometric form. Experimental observations concerning steric restraints germane to thioether donor atoms in other

TABLE I
Electronic spectra for $Co(QS)X^{2+}$ complexes

Compound	λ_{max}nm (ε, m^{-1} cm^{-1})[a]
$Co(QS)Br^{2+}$	566(364), 370(790)[b], 299(14,960), 218(9,220)
$Co(QS)Cl^{2+}$	548(351), 380(390)[b], 288(15,440), 224(9,990)
$Co(QS)N_3{}^{2+}$	536(1,150), 345(8,530), 280(11,630), 217(12,710)
$Co(QS)NCS^{2+}$	529(962), 358(1,954), 286(13,580)
$Co(QS)NO_2{}^{2+}$	478(457), 356(1,500), 283(15,900), 207(11,000)

[a] Spectra determined in water at 20°C.

[b] Shoulder on side of strong UV absorption bond.

systems[5,6,12,16] indicates the isolated series would most favorably adopt the $\alpha\alpha$ configuration.

Continued work in this laboratory will examine the stereospecificity of QS in conjunction with substitution reactions and electron transfer processess at metal centers.

REFERENCES

1. The ligand is abbreviated QS, signifying a sulfur containing quinquedentate ligand.
2. D. A. House and C. S. Garner, *Inorg. Chem.*, 5, 2097 (1966); *Inorg. Chem.*, 6, 272 (1967); *Inorg. Chem.*, 6, 1071 (1967).
3. J. M. Palmer and E. Deutsch, *Inorg. Chem.*, 14, 17 (1975).
4. R. A. Goddard and J. H. Worrell, *Inorg. Chem.*, 16, 1249 (1977).
5. J. H. Worrell and D. H. Busch, *Inorg. Chem.*, 8, 1563 (1969); *Inorg. Chem.*, 8, 1572 (1969).
6. J. H. Worrell, T. E. MacDermott and D. H. Busch, *J. Amer. Chem. Soc.*, 92, 3317 (1970).
7. The solid was not analyzed for C, H, N, however, electronic spectra, ion-exchange and chemical tests for Co(II) demonstrated the presence of $Co(QS)X^{2+}$ and $CoCl_4^{2+}$. The solid may be isolated as the $CoCl_4^{-2}$, $ZnCl_4^{2-}$ or $CoBr_4^{2-}$ salt depending upon mode of preparation. We found it most convenient to convert the above salts directly to the type $[Co(QS)X](ClO_4)_2$, for which elemental analyses are given.
8. Also known as 1,4,7,10,13-pentaazatridecane and abbreviated tetraen and/or tetren.
9. A. M. Sargeson and G. H. Searle, *Nature*, 200, 356 (1963).
10. D. A. Buckingham and D. Jones, *Inorg. Chem.*, 4, 1837 (1965).
11. M. R. Snow, *J. Amer. Chem. Soc.*, 92, 3610 (1970).
12. B. Bosnich, W. R. Kneen and A. T. Phillip, *Inorg. Chem.*, 8, 2567 (1969).
13. G. R. Brubaker, D. P. Schaeffer, J. H. Worrell and J. I. Legg, *Coord. Chem. Rev.*, 7, 161 (1971).
14. *Infrared Spectra of Inorganic and Coordination Compounds* by K. Nakamoto, John Wiley & Sons, NY (1963) pp. 155, 173, 176.
15. R. C. Buckley and J. G. Wardeska, *Inorg. Chem.*, 11, 1723 (1972).
16. J. F. Richardson and N. C. Payne, *Inorg. Chem.*, 17, 2111 (1978).