

complexes with chelated bidentate phosphine ligands. The observed large positive ΔR values for the complexes with five-membered chelate rings and the negative ring contribution for $[\text{Au}(\text{dppp})_2]^+$ are fully consistent with the previously reported trends for five- and six-membered chelate rings.²²

The observation of a deceptively simple singlet in the ^{31}P NMR spectrum of the mixed-ligand complex $[\text{Au}(\text{eppe})_2]^+$ is interpretable as an AA'BB' spin system in which the values of $J(\text{AB})$ (i.e. $^3J[^{31}\text{P}(\text{Ph}_2)-^{31}\text{P}(\text{Et})]$) and $\nu_A - \nu_B$ are both very small. The $^3J[^{31}\text{P}(\text{Ph}_2)-^{31}\text{P}(\text{Et}_2)]$ coupling constants in eppe and $[(\text{AuCl})_2(\text{eppe})]$ are 26 and 53 Hz, respectively. It seems reasonable that this coupling could be very small in the chelated complex in view of previous observations for metal phosphine complexes containing five-membered chelate rings.²³ $^{31}\text{P}-^{31}\text{P}$ spin-spin coupling in a chelate ring can be divided into "through the backbone" and "through the metal" contributions. For a five-membered ring these contributions are nearly equal but of opposite sign, resulting in a small overall value for $J(\text{PP})$.²³

Conclusion

Tetrahedral bis(bis(phosphine))gold(I) complexes, $[\text{Au}(\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}'_2)_2]^+$, containing five- and six-membered chelate rings ($n = 2$ or 3), exhibit a remarkably high kinetic and thermodynamic

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stability. Those containing phenyl substituents are present even in solutions containing low Au(I):ligand ratios (<1:1). Four- or seven-membered chelate rings were not detected in solution by our ^{31}P NMR studies. These ligands give rise to annular (digold) and polymeric species.

Definitive evidence for the existence in solution of the 10-membered annular complex was obtained from detailed NMR studies of the 1:1 Au(I):eppe complex $[\text{Au}_2(\text{Et}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_2]^{2+}$. In D_2O , the $\text{Et}_2\text{P}-\text{Au}-\text{PPh}_2$ isomer predominated (by 2:1) over the $\text{Ph}_2\text{P}-\text{Au}-\text{PPh}_2$ isomer.

Chelation may be a more important feature of the chemistry of Au(I) than has hitherto been supposed. There appears to be an intriguing interplay between the stabilities of two-, three-, and four-coordinate complexes, influenced by steric and electronic factors, and also solvent effects.

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Registry No. Ia, 37095-27-5; Ib, 18024-34-5; Ic, 72428-60-5; Id, 63640-04-0; Ie, 64645-30-3; If, 99350-19-3; Ig, 83543-39-9; IIa, 64466-40-6; IIc, 103852-24-0; IIg, 91382-24-0; IIIb, 19624-67-0; IIIc, 102407-39-6; IIIe, 102532-72-9; IIIf, 100082-39-1; IIIf, 103852-25-1; $[\text{Au}(\text{depe})_2]\text{PF}_6$, 102428-66-0; $[\text{Au}_2(\text{eppe})_2]^{2+}$ (isomer X), 103852-22-8; $[\text{Au}_2(\text{eppe})_2]^{2+}$ (isomer Y), 103852-23-9; $\text{Na}[\text{AuCl}_4]$, 15189-51-2; SbF_6^- , 17111-95-4; PF_6^- , 16919-18-9.

Supplementary Material Available: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Au}(\text{eppe})_2]\text{Cl}$ (IIIc) at 24.2 and 101.3 MHz (1 page). Ordering information is given on any current masthead page.

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Cobalt(II) Bis(1,4,7-trithiacyclonane): A Low-Spin Octahedral Complex

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Cobalt(II) forms a bis complex with 1,4,7-trithiacyclonane (1,4,7-TTCN) with an unprecedentedly large overall formation constant of 8×10^{13} . This complex has an effective magnetic susceptibility of $1.71 \mu_B$. Thus, this is a low-spin octahedral Co(II) complex, and such complexes are exceedingly rare. Cyclic voltammetry of $\text{Co}(1,4,7\text{-TTCN})_2^{2+}$ shows three diffusion-controlled one-electron steps at 0.573, -0.292, and -0.998 V vs. SHE corresponding to Co(III)/Co(II) , Co(II)/Co(I) , and Co(I)/Co(0) reductions, respectively. The unique properties of this complex are suggested to be due to ligand conformational control.

Introduction

Thioethers have been widely regarded as rather poor ligands for the coordination of transition metals.^{1,2} However, the involvement of thioethers as ligands in cytochromes *c* and certain "blue copper" proteins has inspired more detailed examination of thioether coordination chemistry. A number of macrocyclic polythioether complexes have been examined. These have tended to be tetrathioethers,³⁻⁵ forming four-coordinate complexes or five- and six-coordinate complexes with another ligand. In particular we have focused on medium-sized ring polythioethers (crown thioethers) and their interactions with transition metals. Recently we reported on the preparation and structures of bis 1,4,7-trithiacyclonane (1,4,7-TTCN) complexes of Ni(II), Cu(II), and Co(II).⁶ In each complex the metal atom is found in a slightly distorted octahedral environment consisting of two facially coordinated 1,4,7-TTCN ligands. Our previous structural studies of the ligand⁷ revealed a conformation in which all three sulfur atoms

are endodentate and are well-positioned for tridentate coordination, suggesting the possibility of forming unusually stable complexes.

Cobalt complexes of thioethers have not been extensively studied. Only one monodentate thioether complex⁸ and three bidentate thioether complexes⁹⁻¹¹ have been reported. These are all high-spin Co(II). In studies of mixed-donor Co(II) complexes, it becomes apparent that thioethers allow a high degree of inner-sphere reactivity.¹²⁻¹⁵ These complexes are high-spin octahedral Co(II) but seem to be in a close equilibrium with tetrahedral structures, which is not surprising since the energy difference between the two states is less for a d^7 system than for any other first-row transition metal. Low-spin Co(II) complexes are rare and tend to be four- or five-coordinate.¹⁶

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Attempts to prepare low-spin Co(II) complexes of linear tetraethioethers have been marginally successful and have produced high-spin Co(II) ($\mu_{\text{eff}} > 4.9 \mu_{\text{B}}$).^{17,18} Substitution of some of the thioether moieties by phosphorus (PhP) gave greater success and produced low-spin complexes ($\mu_{\text{eff}} = 1.98 - 2.13 \mu_{\text{B}}$).¹⁹ Macrocyclic tetraethioethers have been used with greater success, and reported magnetic moments for the Co(II) complexes are on the order of $3.0 \mu_{\text{B}}$ or lower, possibly indicating high-spin-low-spin crossover.^{19,20} A Co(III) macrocyclic polythioether complex is also reported.²¹ The stability constants of these complexes were only marginally higher than those formed by mono- and bidentate thioether ligands and failed to demonstrate the improved stability that would be expected for macrocyclic chelates. The reason for this no doubt lies in the fact that all donor atoms are exodentate, which necessitates a conformational change in the ligand for coordination to occur. Copper and co-workers²² have recently reported on the octahedral hexathia-18-crown-6 complex of Co(II). This proved to be one of the few examples of low-spin Co(II) ($\mu_{\text{eff}} = 1.8$), although there is considerable tetragonal distortion from octahedral symmetry. Our previous studies of Co^{II}(1,4,7-TTCN)₂²⁺ showed minimal tetragonal distortion and uniformly short Co-S bond distances. These observations prompted the more detailed magnetic, spectroscopic, and electrochemical studies of this unusual complex reported here.

Experimental Section

Materials. The tetrafluoroborate salt of Co(II) was obtained from Alfa/Ventron Products in AR grade; tetrabutylammonium tetrafluoroborate (TBAFB) and tetrabutylammonium hexafluorophosphate (TBAFP) were obtained from Fluka Chemical Corp. and recrystallized from ethanol prior to use. Spectrograde acetonitrile (Burdick and Jackson) was doubly distilled from P₂O₁₀. Mn²⁺ in CaO, used as a magnetic standard, was obtained by heating calcite deposited from seawater at 850 °C under an inert atmosphere. All other reagents were AR grade or better and were used without further purification. The Co^{II}(1,4,7-TTCN)₂²⁺ complex, where 1,4,7-TTCN is 1,4,7-trithiacyclonane, was prepared as described previously.²³

Electrochemical Measurements. Cyclic voltammetric measurements were made with a computer-controlled data acquisition system described previously.²⁴ A Ag/0.1 M AgNO₃ reference electrode in acetonitrile was used for all experiments. This electrode was found to have a potential of 0.592 V vs. NHE. The indicating electrode was a 1.2 cm² platinum flag, and the measurements were made in 0.1 M solutions of TBAFB or TBAFP. A Princeton Applied Research Model 373 digital coulometer was used for controlled-potential electrolysis (CPE) along with a Pine Instruments PIR rotator and DT6 Pt rotating ring-disk electrode (RDE). This electrode was also used for making diffusion coefficient measurements. Cyclic voltammetric data were analyzed theoretically with use of an interactive graphics-based system described elsewhere.^{24,25}

Magnetic Measurements. EPR spectroscopy was performed with a modified Varian Model V-4502 EPR spectrometer described elsewhere.²⁶ It was interfaced to a PDP/8 computer with 32K core memory and a Nicolet EPR software package. A power meter was used to monitor the incident power to the TE₁₀₄ cavity. The temperature was controlled by a thermostated liquid-nitrogen purge system.

Magnetic susceptibility measurements were carried out on a Faraday balance by the method of Inoue.²⁷ The temperature was monitored from 77 to 298 K.

Determination of Formation Constant. Spectrophotometric data were obtained on a Varian Cary 219 spectrophotometer interfaced to a Hew-

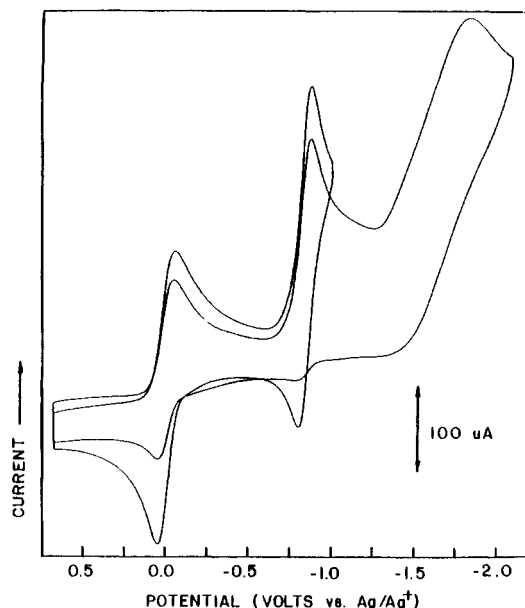


Figure 1. Cyclic voltammogram of 1.5 mM Co(TTCN)₂²⁺ (electrolyte 0.1 M TBAFP in acetonitrile, platinum-flag working electrode potentials vs. NHE).

lett-Packard 2100 A minicomputer and were used to determine the two successive formation constants for the Co^{II}(1,4,7-TTCN)₂(BF₄)₂ complex. A gradient search method²⁸ was used to determine the best fit for the variation of the complex absorbance with total ligand concentration.

Results and Discussion

Electrochemistry of the Co(TTCN)₂²⁺ Complex. Cyclic voltammetry of the Co(II) solution yields three diffusion-controlled one-electron steps with waves at 0.573, -0.292, and -0.998 V vs. the standard hydrogen electrode (SHE). It has been established that the three waves correspond to Co(III)/Co(II), Co(II)/Co(I), and Co(I)/Co(0) reductions, respectively. Current-voltage curves obtained at the Pt RDE confirm the conclusions from cyclic voltammetry and indicate that the bulk-solution species is indeed the Co(II) complex. Figure 1 shows the voltammogram of the Co(III)/Co(II) and Co(II)/Co(I) waves, which are found to have E° values of 0.019 and -0.748 V vs. Ag/Ag⁺ reference and standard heterogeneous electron-transfer rates of 0.01 and 0.0075 cm²s⁻¹, respectively. Controlled-potential reduction of the Co(II) complex yielded a Co(I) complex that could be reversibly oxidized to the starting material. The Co(I)/Co(0) reduction step is irreversible, and cyclic voltammetry suggests the release of the ligand as the result.

The anodic current corresponding to Co(I)/Co(II) oxidation is not as large as the corresponding reduction current at slow scan rates; however, oxidation current approaches reduction current as the scan rate is increased. This is evidence for a chemical step following the Co(II)/Co(I) electron transfer. This wave can be fitted at all scan rates if a following reversible chemical step with $K_{\text{eq}} = 2.0$ is introduced into the algorithm. The product of this chemical step has not been identified but is postulated to be a change in coordination geometry of Co(I) since the controlled-potential electrolysis is reversible. It does not appear to be a second or higher order interaction as there is no measurable concentration effect on peak currents.

Magnetic Properties of the Bis Complex. Co(TTCN)₂(BF₄)₂ is paramagnetic as determined by EPR and magnetic susceptibility measurements, $\mu_{\text{eff}} = 1.71 \mu_{\text{B}}$, and is temperature independent down to 77 K. The Curie temperature was calculated from the normalized double integral of the EPR signal as determined between 77 and 360 K and found to be -5 K. A calculated Curie temperature below absolute zero is evidence that the metal nuclei were not close enough together for intermolecular magnetic in-

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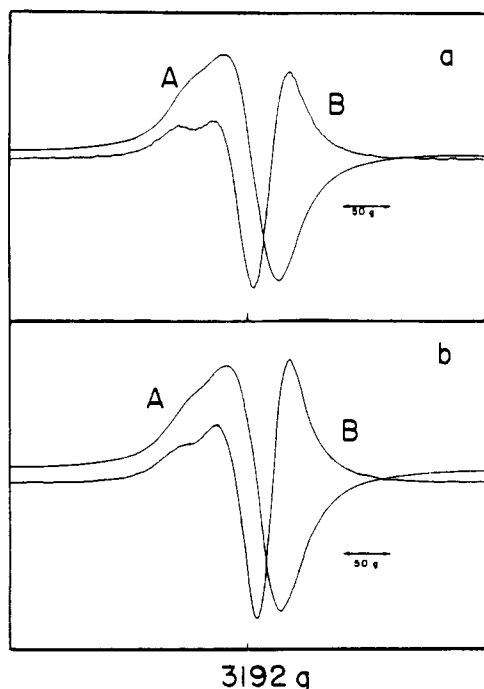


Figure 2. Solid-phase EPR spectra for $\text{Co}(\text{TTCN})_2(\text{BF}_4)_2$ (curve A, first-derivative spectrum; curve B, second-derivative spectrum): (a) = -43°C ; (b) = -150°C .

teractions to occur. This behavior is predicted by the metal-metal distances observed in the X-ray crystallographic data. The g_{av} value of 2.089 for the cobalt complex was obtained from the solid-phase spectra (Figure 2). It is not possible from these spectra to calculate g_{\parallel} , but it is evidently very close to g_{\perp} . The value of the electron spin s was found to be 0.50 for cobalt.

The low-spin character of the cobalt complex is consistent with a d-d transition at 478 nm ($\epsilon = 93$).⁶

Our previously published values appear to be in error. Re-measurement resulted in the $\lambda_{\text{m}}(\text{CH}_3\text{NO}_2)$ parameters 478 ($\epsilon = 76$), 335 (7000), and 262 (7300) nm with shoulders at 555 and 279 nm and a very weak band around 700 nm. A similar spectrum was obtained in acetonitrile solution with $\lambda_{\text{m}}(\text{CH}_3\text{CN})$ 476 (100), 335 (7300), and 260 (7400) nm and shoulders at 560 and 279 nm.

The solution EPR spectrum consists of the expected eight lines for cobalt ($I = 7/2$; Figures 2 and 3). The line width is 20.2 G, and $g_{\text{av}} = 2.067$, which gives evidence of some tetragonal distortion of the complex. A low-spin octahedral complex of Co(II) would be expected to exhibit axial compression due to the Jahn-Teller effect since by having a single e_g electron it is in a 2E_g ground state. The shift in g value on solvation toward g_e indicates that the ligand is strongly bonded in solution and is having a quenching effect on the orbital angular momentum of the unpaired electron.

Formation Constants. Formation constants in acetonitrile for the first and second steps were found to be $K_1 = (9.2 \pm 0.1) \times 10^6$ and $K_2 = (1.0 \pm 0.1) \times 10^7$, for a K_f (overall) value of $(9.2 \pm 0.1) \times 10^{13}$, 4 orders of magnitude or more higher than other reported formation constants of thioether-cobalt complexes.²⁹⁻³³ This indicates great enhancement of complex stability, probably due at least partly to the fact that the conformation of the free ligand is essentially unaltered on complexation. This would be reflected in a more favorable overall ΔG for the complexation.

In sum our studies reveal that 1,4,7-TTCN is an unprecedentedly good ligand for cobalt(II) and the bis complex has un-

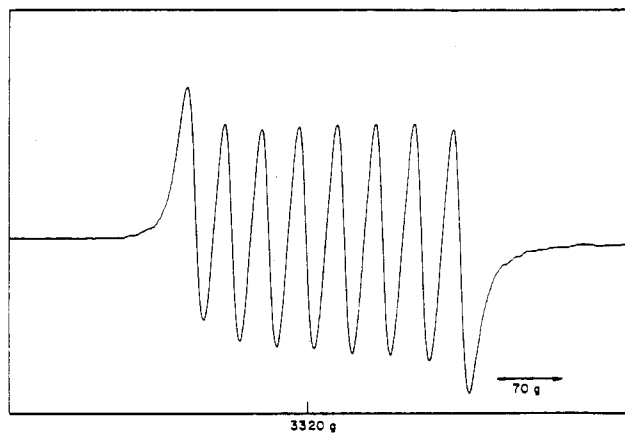


Figure 3. First-derivative EPR spectrum for aqueous $\text{Co}(\text{TTCN})_2^{2+}$ (quartz flat cell, ambient temperature).

usual properties. Although the coordination geometry about the metal ion in $\text{Co}^{\text{II}}(1,4,7\text{-TTCN})_2$ is octahedral, it is a low-spin complex. Hartman et al.²² reported that the coordination geometry about the cobalt ion in the Co(II) complex of hexathia-18-crown-6 is octahedral and it is also low spin. Three possible reasons were offered for this result, namely, that the ligand field strength of thioethers is much greater than previously believed, thioethers greatly decrease the spin-pairing energy (nephelauxetic effect), or ligand conformational effects result in unusually short metal ion bonds and metamorphosis of a weak-field ligand into a strong-field ligand. In support of this last suggestion Hintsa et al.³⁴ found unusually short metal-sulfur interatomic distances in the Ni(II) complex of hexathia-18-crown-6. The structure of this complex was said to be determined in the following way: The nickel ion determined the geometry, but the ligand determined the Ni-S bond lengths. Our $\text{Co}^{\text{II}}(1,4,7\text{-TTCN})_2$ complex shows bond lengths shorter than those measured by Cooper et al.²² Whereas $\text{Co}^{\text{II}}(\text{hexathia-18-crown-6})$ shows tetragonal distortion in which the equatorial bond lengths are shorter than the axial ones, the reverse pattern obtains with our complex. In $\text{Co}^{\text{II}}(1,4,7\text{-TTCN})_2$ the axial bonds are compressed from the calculated sum of covalent radii of 2.360 to 2.240 Å but the equatorial bonds are the sum of the calculated covalent radii (2.356–2.367 Å). Whether our geometry represents an average of more distorted geometries or an overwhelming of the Jahn-Teller stabilization energy remains to be seen. Nevertheless, our results require the reassessment of thioethers as metal ligands. Of potentially greatest importance is ligand conformational control of metal ion complex properties. That is, conformational change of 1,4,7-TTCN may require higher energy than Jahn-Teller stabilization obtained on distortion of the complex. Metal ions, when coordinated to proteins, often bind strongly and show unprecedented behavior. One reason may be conformational rigidity in the protein that is unchanged on complexation. Our results provide an indication that ligand conformational control of metal ion complexes may be realizable with the relatively simple ligand 1,4,7-TTCN.³⁵

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Registry No. $\text{Co}(\text{TTCN})_2(\text{BF}_4)_2$, 83650-38-8; $\text{Co}(\text{TTCN})_2^{3+}$, 97391-16-7; $\text{Co}(\text{TTCN})_2^+$, 97391-15-6; $\text{Co}(\text{TTCN})_2$, 103904-48-9.

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 (35) Subsequent to the original submission of our paper, a paper by Wieghardt et al. (*Inorg. Chem.* **1985**, *24*, 3067–3071) reported their magnetic susceptibility measurements on $\text{Co}(1,4,7\text{-TTCN})_2(\text{BF}_4)_2$ which indicate that it is a low-spin complex, in agreement with our work.