Synthesis and Characterization of Niobium(III) and Tantalum(III) Dimers with Bidentate Ligands

M. E. CLAY and T. M. BROWN*

Bateman Science Center, Department of Chemistry, Arizona State University, Tempe, Ari. 85287, U.S.A.

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The reaction of $M_2Cl_6 \cdot 3THT$ (M = Nb, Ta; THT = tetrahydrothiophene) with various bidentate ligands has been investigated. New molecular species of the type $M_2Cl_6 \cdot 2B$ [M = Nb, Ta; B = 2,5-dithiahexane, 3,6-dithiaoctane, 2,2′-bipyridine or ethylenebis(diphenylphosphine)] have been isolated in good yields. The ethylenebis(diphenylphosphine) complex of niobium has been reinvestigated and the results are compared to those reported previously. All of the complexes were characterized by chemical analysis, IR, ESR and magnetic susceptibility data. Each of the new complexes show some degree of metal–metal interaction which increases with decreasing temperature.

Introduction

In recent years, investigators have established that many early transition metal dimers contain strong metal–metal interactions. Initially, work focused on Groups VIB and VIIB with an emphasis on complexes of molybdenum and rhenium [1, 2]. More recently, metal dimer chemistry was expanded into group VB when complexes of the formula $M_2X_6 \cdot 3THT$ (X = Cl, Br or I and THT = tetrahydrothiophene) were prepared using both niobium and tantalum [3–6]. To date, however, very little systematic work on the reaction chemistries of these complexes has been published.

In order to investigate these niobium(III) and tantalum(III) systems more thoroughly, a concerted effort was made to prepare bidentate ligand complexes of these two metals in the plus three oxidation state. Special consideration was made for the investigation of changes in bonding between the metal atoms after ligand substitution. A niobium(III) complex previously reported by Allen and Naito [7] was included in this study; however, the results of the present magnetic studies contrasted with their results. Additionally, all of the bidentate ligand substitutions were extended to the tantalum(III) system which to date has remained relatively unexplored.

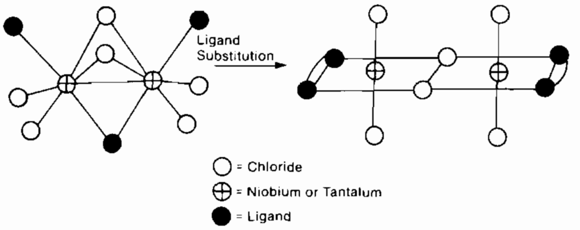

Fig. 1. Proposed structure of $M_2Cl_6B_2$ complexes (M = Nb, Ta, B = bidentate ligand).

Results and Discussion

Synthesis – Properties

All of the new complexes were readily formed at room temperature and found to be insoluble in all non-reactive organic solvents examined. In every case, the three tetrahydrothiophene ligands were replaced by two incoming bidentate ligands and the formation of an insoluble product promoted the reaction. A consideration of available coordination site number and stereochemical symmetries lead to the postulation that the confacial bioctahedral starting complexes rearrange upon ligand substitution into the bioctahedral arrangement previously suggested by Blight *et al.* [8] and subsequently by Allen and Naito [7]. This final structure is illustrated in Fig. 1. Even though no crystallographic evidence is available, the insolubility of these compounds compared to the analogous monodentate ligand compounds is suggestive of a highly symmetrical structure which

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*Author to whom correspondence should be addressed.

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TABLE I. Infrared Bands (cm^{-1}) for Region of 1700–600 cm^{-1}.

Compound	Observed Absorptions
$Nb_2Cl_6(DTH)_2$	1496m, 1416s, 1325w, 1308w, 1265m, 1188vw, 1163vw, 1085w, 1039s, 992s, 975s, 911w, 892w, 862vw, 843m, 811w, 754mw, 728m, 707w, 641m
$Ta_2Cl_6(DTH)_2$	1422vs, 1365w, 1325w, 1300w, 1267m, 1160m, 1033m, 972s, 860s, 832ms, 728m, 655w
$Nb_2Cl_6(DTOC)_2$	1450s, 1410vs, 1380m, 1263m, 1250m, 1145vw, 1068w, 1051w, 1040w, 972m, 901m, 851m, 798m, 782m, 760w, 725w, 650w, 624w
$Ta_2Cl_6(DTOC)_2$	1450m, 1422s, 1408s, 1380ms, 1296w, 1254m, 1055w, 976m, 911w, 860m, 825w, 778s, 722w
$Nb_2Cl_6(BIPY)_2$	1602vs, 1571m, 1543w, 1530w, 1473s, 1442vs, 1319m, 1028m, 940m, 774vs, 733m, 652m, 640m
$Ta_2Cl_6(BIPY)_2$	1608vs, 1575m, 1545w, 1530w, 1478s, 1448vs, 1321m, 1032m, 944m, 773vs, 735s, 660m, 640w
$Nb_2Cl_6(DIPHOS)_2$	1588w, 1575w, 1487ms, 1438s, 1197mw, 1099ms, 1076w,sh, 1030w, 1000w, 865w, 832w, 742ms, 698s, 678w

w = weak, m = medium, s = strong, v = very and sh = shoulder

would promote a very ordered solid state packing arrangement.

While the reported reactions all proceeded rapidly to completion, not all bidentate ligands were found to yield the desired products. Bis(phenylthio)ethane showed no evidence of reactivity with either the niobium or the tantalum tetrahydrothiophene complexes even at 80 °C temperatures over reaction periods of one week. Furthermore, attempts to react ethylenebis(diphenylarsine) and 2,2,7,7-tetramethyl-3,6-dithiaoctane with the metal complexes resulted in the formation of small quantities of precipitate which were non-stoichiometric. On the other hand, the bidentate sulfur ligands 2,5-dithiahexane (DTH) and 3,6-dithiaoctane (DTOC) as well as 2,2′-bipyridine (BIPY) and ethylene bis(diphenylphosphine) (DIPHOS) react completely within a 6–12 hour time period under similar conditions. Thus, it appears that the basicity of the ligand (and possibly the solvent used) is of great importance in displacing the THT ligands already present. On-going studies have indicated that the more basic the ligand the greater is the tendency to react and, in some cases, to even split the dimer during the ligand substitution process [9].

Infrared Spectra

The infrared spectra of the complexes are tabulated from the region of 1600–600 cm^{-1} in Table I. All absorptions in this region correspond to ligand vibrations and, as expected, the infrared spectra for the DTH and DTOC complexes are similar. The infrared spectral characteristics of these ligands have been reported by several investigators [10–13], and the disappearance of the strong free-ligand absorption at 1200 cm^{-1} has been assigned to the coordination of these thioethers in a gauche conformer [10]. Furthermore, a previous study indicated that the gauche conformer was the predominate form in many coordination complexes of these ligands [13].

It is also apparent that the niobium complexes have more complicated spectra than the corresponding tantalum compounds. Hayshi *et al.,* [12] suggested that doublets in the spectra of these ligands often resulted from a mixture of conformers in the coordination spheres of the central metal. A comparison of the infrared spectra with those previously reported for niobium(IV) DTH complexes [13] suggests that the tantalum DTH and DTOC spectra are indicative of these ligands coordinated in the gauche form, while the more complicated niobium spectra may be indicative of mixed ligand conformers.

The observed bands for the DIPHOS complex are normal for this ligand and the spectrum agrees, for the most part, with that previously reported by Allen and Naito [7]. There is, however, a medium strong band at 1099 cm^{-1} which was not reported by these authors and this discrepancy cannot be readily explained. Even so, the spectra of these compounds are similar enough to be considered the same in terms of their ligand absorptions.

The infrared spectra for the BIPY complexes are indicative of strongly coordinated ligands and in agreement with previously reported spectra for similar complexes [14, 15]. The ring vibration modes in the 1600–1400 cm^{-1} region are all shifted and split and a new absorption is observed in the 1300 cm^{-1} region. A similar 1300 cm^{-1} absorption has been observed for coordinated BIPY in uranium and chromium complexes [14]. Additionally, a new band of medium intensity is observed in the 940 cm^{-1} region. Initially, this band was thought to arise from

TABLE II. Infrared Bands (cm^{-1}) for Region of 600–200 cm^{-1}.

Compound	Observed Absorptions
$Nb_2Cl_6(DTH)_2$	475w, 458vw, 402w, 348vs, 302m, 253vw, 208mw
$Ta_2Cl_6(DTH)_2$	492vw, 455w, 438m, 400vw, 323vs, 292m, 209w
$Nb_2Cl_6(DTOC)_2$	480m(broad), 461w, 387w, 346vs, 293m, 258w, 230vw, 214vw
$Ta_2Cl_6(DTOC)_2$	570vw, 490vw, 458w, 432m, 396w, 322vs, 290s, 211w
$Nb_2Cl_6(BIPY)_2$	470mw, 427w, 400w, 349s,sh, 323vs, 289ms, 260w, 208 broad
$Ta_2Cl_6(BIPY)_2$	505w, 487vw, 472vw, 398w, 310 broad, 230vs,sh, 212m
$Nb_2Cl_6(DIPHOS)_2$	547w, 522s, 500sh, 490m, 480sh, 436w, 417w, 345vs, 292m, 258w, 202m

w = weak, m = medium, s = strong, v = very, sh = shoulder.

TABLE III. Magnetic Susceptibility Data for Niobium(III) and Tantalum(III) Dimers.

Compound	(Temp.) K	10^6 χ_m[a]	10^6 χ_D	10^6 χ_{corr}	μ_{eff}/M (B.M.)
$Nb_2Cl_6(DTH)_2$	(298)	585	−341	926	0.75
	(84)	864	−341	1200	0.45
$Nb_2Cl_6(DTOC)_2$	(298)	418	−388	806	0.70
	(84)	1190	−388	1580	0.52
$Nb_2Cl_6(BIPY)_2$	(298)	970	−276	1247	0.87
	(84)	1430	−276	1710	0.54
$Nb_2Cl_6(DIPHOS)_2$	(298)	−193	−678	485	0.54
	(84)	966	−678	1644	0.53
$Nb_2Cl_6(THT)_3$	(298)			198	0.34
$Ta_2Cl_6(DTH)_2$	(298)	289	−353	642	0.62
	(84)	1070	−353	1423	0.49
$Ta_2Cl_6(DTOC)_2$	(298)	282	−401	683	0.64
	(84)	691	−401	1090	0.43
$Ta_2Cl_6(BIPY)_2$	(298)	−149	−396	247	0.39
	(84)	166	−396	562	0.31
$Ta_2Cl_6(THT)_3$	(298)	−276	−371	95.0	

[a] χ_M = molar susceptibility, χ_D = diamagnetic correction, $\chi_{Corr} = \chi_M - \chi_D$.

oxygen coordinated to the metals, however, since it is in the same position for both of the metals this possibility is unlikely. Moreover, complexes of chromium, vanadium and titanium in low oxidation states have similar absorptions [15]. Noting that Li(BIPY) exhibited this characteristic band at 944 cm^{-1}, one investigation group suggested that since the BIPY was negatively charged, this absorption could indicate electron delocalization onto the ligand ring system is present in the new complexes.

The far-infrared absorptions are listed in Table II for the region which contains the infrared active metal–ligand bands including the metal-halide stretching mode. This major metal–halide absorption is identifiable in each case since the large dipole moment of this bond produces an intense absorption band. The niobium–THT dimer has this absorption at 341 cm^{-1} while that of the tantalum–THT dimer is at 320 cm^{-1} [3, 5]. The new sulfur and phosphorus ligand complexes have metal–halide absorptions similar to the parent $M_2Cl_6(THT)_3$ complexes. The nitrogen ligand complexes both have lowered metal–halide absorptions. This is suggestive that some electronic differences are present in the nitrogen ligand complexes, and very possibly relates to the ability of these ligands to accept electron delocalization from the metals into the pi systems of the rings. Furthermore, these slight electronic differences appear in the infrared spectra, the magnetic susceptibility measurements and the EPR spectra.

A final observation about this region is that the THT ligands have been totally replaced in the new complexes. The characteristic absorptions of this

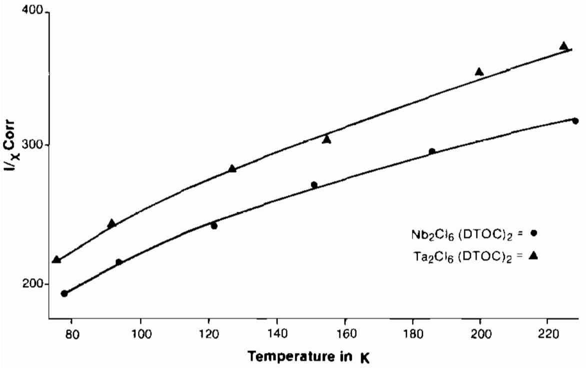

Fig. 2. $1/\chi_{corr}$ *vs.* temperature for the DTOC dimers of niobium and tantalum.

ligand at 230 and 320 cm^{-1} are absent and in general this spectral region is simplified. The loss of the bridging THT resulting in the structural rearrangement shown in Fig. 1 would be likely to produce the observed spectrum simplification and since $NbCl_5$ and $TaCl_5$ both adopt this geometry in the solid state, it is not an unlikely arrangement.

Magnetic Susceptibility Measurements

As is seen in Table III, the bidentate ligand complexes all exhibit temperature dependent paramagnetism, while previously reported niobium(III) and tantalum(III) dimers (including Nb_2Cl_6-$(DIPHOS)_2$) have all been diamagnetic with small TIP contributions [3, 5, 7]. Since the susceptibility was observed to be temperature dependent in these new complexes, a temperature study was undertaken on two of the complexes. The curves which resulted are shown in Fig. 2. Both of the complexes deviate from Curie–Weiss behavior and the tantalum complex has a lower magnetic moment presumably because of increased spin–orbit coupling and increased metal–metal interactions.

The curvature observed for these two complexes is not surprising, however, since the metal atoms within the dimeric units are probably still strongly interacting. Dimers with close metal centers such as $Cu_2(acetate)_4$ often exhibit increased anti-ferromagnetic interactions at lower temperatures [16]. Similar, spin pairing of electrons at lower temperatures could easily account for the observed line curvature. Furthermore, even monomeric niobium(IV) salts have displayed a line curvature so the probability of a similar deviation in the dimeric systems is greatly increased [20]. The data curvature prevents an accurate estimation of the TIP contributions of the systems; however, it can reasonably be estimated as 30 to 40% of the observed moments by comparison to the original dimeric units for which TIP was apparent [3, 5].

The effective magnetic moments all lie within the range reported for niobium(IV) and tantalum(IV) d^1 systems [17–20]. Moments of this magnitude are exactly what would be predicted for a d^2 dimer with a single bond between the metal atoms. It is currently postulated that one of the original bonds is disrupted during the ligand substitution and subsequent molecular geometry change while the other bond remains intact. The observed magnetism is then presumably lowered by spin–orbit coupling and/or antiferromagnetic interactions between the adjacent metal atoms. As a comparison, moment values of 1.41 B.M. and 0.70 B.M. have been reported for the respective complexes $NbCl_4(BIPY)$ and $TaCl_4(BIPY)$ [19]. These values correspond to 0.87 B.M. and 0.39 B.M. for the complexes $Nb_2Cl_6(BIPY)_2$ and Ta_2Cl_6-$(BIPY)_2$, respectively.

EPR Measurements

Electron paramagnetic resonance spectra were taken in order to confirm that the observed paramagnetic behavior of these complexes was due to unpaired electrons. EPR investigations have shown that the original THT dimers produce no observable signals even at elevated instrument sensitivities, while the bidentate ligand substituted complexes all gave easily observable spectra at room temperature. The average g-factors and other spectral parameters are tabulated in Table IV. Since the spectra were all run on solid samples, the expected 10 and 7 line hyperfine splitting patterns for niobium and tantalum were not resolved; however, there were several unexpected differences in the spectra.

The spectra for the niobium complexes of DTH, DTOC and DIPHOS are all broad single lines while the BIPY complex has observable hyperfine bands. This latter spectrum is not unlike the spectrum recorded for the $Nb(OCH_3Cl_5^{2-}$ ion at liquid nitrogen temperature [21]. The tantalum DTH and DTOC complexes gave almost identical spectra with similar g-values and their line shapes are somewhat more complex than those observed for the analogous niobium compounds. In contrast, the tantalum BIPY compound has a less complex hyperfine pattern than its niobium analogue. Although these spectra are not readily interpretable chemically, they do suggest the possibility of a wider electronic variability among the complexes than might naively be assumed. Unfortunately, there has not been a great deal of EPR data taken for second and third row transition metal compounds so extensive comparisons of these systems is not possible at this time. Finally, it is apparent that the niobium complexes have g-values closer to the free electron value of 2.0 than the tantalum compounds. This would be the expected result if the tantalum compounds have a greater spin–orbit coupling interaction and is in agreement with the

TABLE IV. Data for the EPR Spectra of the Nb(III) and Ta(III) Dimers.

Compound	Sweep Width	Spectrum Width	g Value	p–p Width
$Nb_2Cl_6(DTH)_2$	5 kG	~2300 G	1.96	240 G
$Nb_2Cl_6(DTOC)_2$	10 kG	~2000 G	2.00	559 G
$Nb_2Cl_6(DIPHOS)_2$	5 kG	~2000 G	1.98	743 G
$Na_2Cl_6(BIPY)_2$	5 kG	~2300 G	2.04	– complex hyperfine
$Ta_2Cl_6(DTH)_2$	2.5 kG	~1000 G	1.85	453 G (complex peak)
$Ta_2Cl_6(DTOC)_2$	2.5 kG	~1200 G	1.83	443 G (complex peak)
$Ta_2Cl_6(BIPY)_2$	2.5 kG	~1100 G	1.99	– complex hyperfine

observed magnetic data for the complexes. Although these values are not equivalent, they are roughly comparable given the possibility of interactions between adjacent metal centers in the dimers. Thus, the differences between the compounds possibly arise from increased electronic interactions within the dimeric systems.

Experimental

General

The complexes described in this paper were extremely sensitive to air and moisture. Thus, all manipulations and characterizations were carried out on a vacuum manifold or in an inert nitrogen atmosphere. The starting complexes, $Nb_2Cl_6(THT)_3$ and $Ta_2Cl_6(THT)_3$ were prepared using procedures previously described by McCarley and coworkers [3–6].

The solvents were dried and outgassed over P_2O_5 before being vacuum distilled onto outgassed Linde 4A molecular sieves for storage. The liquid ligands were dried and stored in a similar manner. The solid ligands were purified by standard methods before being dried and outgassed on the vacuum line [22]. Manipulations of solids were then carried out in a nitrogen filled glove box.

Complex Preparations

Since all of the resulting products were insoluble in all non-aqueous solvents tested, preparative methods had to include procedures for the separation and washing of the final precipitates. Moreover, since recrystallization of the products was impossible several of the complexes were slightly impure; however, this never gave any indication of being a large enough factor to effect the bulk properties of the complexes. The yields of the reactions were determined to be quantitative so that the lower yields are reflections of product loss during transferring and cleaning procedures.

Bis(2,5-dithiahexane)hexachlorodiniobium(III)

$Nb_2Cl_6(DTH)_2$, was formed by mixing 0.30 g (0.45 mmol) of $Nb_2Cl_6(THT)_3$ with approximately 5 ml of 2,5-dithiahexane in a round bottom flask. Thirty ml of toluene was added under a vacuum to serve as a solvent. After stirring for 12 hours at room temperature the insoluble red solid was filtered and washed with toluene and cyclohexane in a solvent box before being vacuum dried at 25 °C for 48 hours. The recovered yield was typically 0.30 g of red solid. *Anal.* Calcd. for $Nb_2Cl_6(C_4H_{10}S_2)_2$: C, 14.95; H, 3.14; Cl, 33.08. Found: C, 14.77; H, 2.94; Cl, 32.54.

Bis(2,5-dithiahexane)hexachloroditantalum(III)

$Ta_2Cl_6(DTH)_2$, was prepared in an analogous manner to the similar niobium complex. Typically 0.40 g (0.48 mmol) of $Ta_2Cl_6(THT)_3$ and approximately 5 ml of 2,5-dithiahexane were allowed to react for 12 hours. The final product was a dark green powder and 0.35 g was recovered. *Anal.* Calcd. for $Ta_2Cl_6(C_4H_{10}S_2)_2$: C, 11.73; H, 2.47; Cl, 25.97. Found: C, 11.73; H, 2.21; Cl, 25.14.

Bis(3,6-dithiaoctane)hexachlorodiniobium(III)

$Nb_2Cl_6(DTOC)_2$ was prepared by adding 0.30 g (0.45 mmol) of $Nb_2Cl_6(THT)_3$ to a flask and distilling about 3 ml of 3,6-dithiaoctane into the flask. After adding 30 ml of toluene the mixture was stirred for 12 hours at room temperature. The resulting precipitate was washed with toluene and cyclohexane in the solvent box before being dried under a vacuum at room temperature for 48 hours. The yield was 0.31 g of red powder. *Anal.* Calcd. for $Nb_2Cl_6(C_6H_{14}S_2)_2$: C, 20.61; H, 4.04; Cl, 30.42. Found: C, 19.61; H, 3.59; Cl, 29.20.

Bis(3,6-dithiaoctane)hexachloroditantalum(III)

$Ta_2Cl_6(DTOC)_2$ was prepared analogously to the similar niobium complex above. For the reaction of 0.40 g (0.48 mmol of $Ta_2Cl_6(THT)_3$ with 3 ml of 3,6-dithiaoctane 0.33 g of light green solid was recovered. *Anal.* Calcd for $Ta_2Cl_6(C_6H_{14}S_2)_2$: C, 16.47; H, 3.23; Cl, 24.30. Found: C, 15.55; H, 2.58; Cl, 23.90.

Bis(ethylene bis(diphenylphosphine)(hexachlorodiniobium(III))

$Nb_2Cl_6(DIPHOS)_2$ was formed in a filtering reaction vessel by the reaction of 0.30 g (0.45 mmol) of $Nb_2Cl_6(THT)_3$ with 0.54 g (1.36 mmol) of DIPHOS using 30 ml of toluene as solvent. After stirring the mixture at room temperature for 12 hours the vessel was inverted to filter the light purple precipitate. The excess DIPHOS was washed out of the product by extraction with toluene followed by pentane. After vacuum drying the solid at room temperature for 48 hours 0.32 g of light purple solid was recovered. *Anal.* Calcd for $Nb_2Cl_6(C_{26}H_{24}P_2)_2$: C, 52.24; H, 4.06; Cl, 17.79. Found: C, 51.86; H, 4.06; Cl, 17.12.

Bis(2,2'-bipyridine)hexachlorodiniobium(III)

$Na_2Cl_6(BIPY)_2$ was synthesized by reacting 0.40 g (0.60 mmol) of $Nb_2Cl_6(THT)_3$ with 0.21 g (1.3 mmol) of BIPY in 30 ml of toluene. The reaction was carried out in an evacuated reaction vessel, which was inverted to filter the product which formed after stirring the mixture at room temperature for 12 hours. The dark blue precipitate was then extracted with toluene and vacuum dried at 60 °C for 48 hours in order to remove any excess BIPY. The recovered yield of dark blue powder was 0.40 g. *Anal.* Calcd for $Nb_2Cl_6(C_{10}H_8N_2)_2$: C, 33.79; H, 2.27; Cl, 29.92; N, 7.88. Found: C, 32.96; H, 2.06; Cl, 28.66; N, 7.71.

Bis(2,2'-bipyridine)hexachloroditantalum(III)

$Ta_2Cl_6(BIPY)_2$ was formed by reacting 0.40 g (0.48 mmol) of $Ta_2Cl_6(THT)_3$ with 0.21 g (1.3 mmol) of BIPY in 30 ml of toluene as described above for the niobium complex. The final yield of vacuum dried dark brown solid was 0.39 g. *Anal.* Calcd for $Ta_2Cl_6(C_{10}H_8N_2)_2$: C, 27.08; H, 1.82, N, 6.31; Cl, 23.98. Found: C, 27.06; H, 1.90; N, 6.41; Cl, 23.35.

Physical Measurements

Elemental analyses were carried out by Galbraith Laboratories, Inc., in Knoxville, Tenn.

The infrared spectra of the compounds were obtained on a Beckman IR-12 spectrometer using samples which had been prepared in a dry box. The spectra were measured using sodium chloride windows and polyethylene plates. Additionally, split mulls using Nujol and Fluorolube were employed in order to remove any interfering bands. Magnetic susceptibility measurements were taken on samples which were sealed in pre-weighted teflon buckets in the glove box. The susceptibilities were measured using a standard Faraday method and the balance was calibrated using $HgCo(NCS)_4$.

The EPR spectra were obtained for solid samples at room temperature (23 °C). All samples were run in sealed quartz tubes to prevent decomposition. The spectrometer was an x-band reflection spectrometer employing a Varian V-4531 microwave cavity and first-derivative signal detection. The magnetic field was calibrated using Fremy's salt and the g-factors were compared to a pure lithium standard. Typically, the spectra were run under the following conditions: microwave frequency, 9.075 GHz; microwave power 30 mV; modulation frequency, 100 KHz; temperature, 296 K and modulation amplitude, .6G.

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