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Coordination of diorganotellurides to cobalt(III) in cobaloximes

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Dedicated to the memory of Michelle Millar whose enthusiasm and spirit brought joy to inorganic chemists everywhere.

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ABSTRACT

The unexpectedly aqueous stable *bis*-tellurium cationic complex $[Co(dmgH)_2[PhTe(CH_2)_3SO_3Na]_2]^*(1^*)$ (dmgH⁻ = dimethylglyoximate) has been fully characterized in the solid state and in solution. The UV-Vis spectrum of 1^{*} differs from that of earlier cobaloximes, exhibiting a new low energy band centered at λ_{max} = 425 nm ($\varepsilon \sim 26155 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and assigned with DFT calculations to allowed LMCT transitions. ¹H, ¹³C, and ¹²⁵Te NMR spectra show unequivocally that two diastereomers exist equally in water, 50% of the achiral C_{2h} meso- $[Co(dmgH)_2[R,S-PhTe(CH_2)_3SO_3Na]_2]^*$ and 50% of the chiral C_2 *rac*- $[Co(dmgH)_2[PhTe(CH_2)_3SO_3Na]_2]^*$ (25% of each enantiomer $[Co(dmgH)_2[R,R-PhTe(CH_2)_3SO_3Na]_2]^*$ and $[Co(dmgH)_2[S,S-PhTe(CH_2)_3SO_3Na]_2]^*$). The solid-state structure of the meso diastereomer has been solved. Neutral mono-tellurium complexes $[CoCl(dmgH)_2[Te(p-MeO-C_6H_4)_2](2)$ and $[CoCl(dpgH)_2$ $[Te(p-MeO-C_6H_4)_2](3) (dpgH⁻ = diphenylglyoximate)$ have also been characterized in the solid (3) state and in solution (2 and 3). The structural results provide the first examples of Co(III)-Te bonds. The solid-state structure of the related cobaloxime salt $[Co(dmgH)_2(py)_2][CoCl_2(dmgH)_2]$ obtained during one synthesis is also reported.

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1. Introduction

In coordination chemistry, the compatibility of different metal ions and ligands for binding has long been noted, with Pearson's analysis of hard and soft acids and bases (HSAB) for metal ions and ligands, respectively, being the most widely cited and employed [1]. In this paper, we report several new Co(III) complexes that possess a divalent telluroether ligand. In the HSAB system, Co(III) is viewed as a "very hard" metal ion while telluroethers (RR'Te) are considered as "very soft". Telluroethers, as well as analogous ligands with Se and S donor atoms, generally exhibit poor ability to coordinate to medium or high oxidation states of 3d transition metals [2]. Whereas there have been several reports previously of Co-Te bonds in organometallic compounds having Co in the +1 oxidation state, the present systems are the first between Co(III) and Te in telluroethers. In light of the metallic nature of tellurium as an element, the Co-Te bonds in this report also represent interesting examples of polarized metal-metal bonding [3].

Our path to the preparation and characterization of the title complexes was circuitous and derived from work that was being done on the visible–light driven generation of H₂ from water, corresponding to the reductive side of water splitting [4]. In these

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studies, systems composed of a light absorber or photosensitizer (PS), a catalyst, aqueous protons and a sacrificial electron source are examined under visible light irradiation for H₂ generation. The photosensitizers may be either metal complexes or organic dves having long-lived excited states for electron transfer. One set of molecular catalysts that has been extensively studied are cobaloxime complexes such as [Co(dmgH)₂LCl], were L is a pyridine or phosphine ligand; these complexes are catalysts for both photochemical and electrochemical production of hydrogen with relatively good levels of activity [4b,5]. In the photochemical studies, the sacrificial donors have generally been tertiary amines such as triethylamine (TEA), triethanolamine (TEOA) and ethylenediamine (tetraacetic acid) (EDTA), that upon oxidation undergo irreversible decomposition through well established chemistry [6]. Another sacrificial donor is ascorbic acid that is used under more acidic conditions (pH 4-5).

The relatively small number of compounds used as sacrificial donors, together with undesirable aspects of their decompositions such as radical formation and/or liberation of a second highly reducing electron prompted us to seek additional compounds that could be easily oxidized as electron donors in hydrogen generating systems. In this regard, Te(II) compounds proved attractive because they can be easily oxidized to Te(IV) and they have been shown to catalytically activate hydrogen peroxide [7]. In the course of initial studies of Te(II) compounds as potential electron sources for hydrogen formation with catalysts such as [Co(dmgH)₂LCI], the formation of strongly colored solutions were seen. Additionally,





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when an unsymmetrical TeRR' compound was examined, evidence of diasteromers was seen by NMR spectroscopy. In fact, coordination of telluroethers bearing different substituents has been reported previously to lead to chirality in complexes of Pd(II), Pt(II) and Ru(II) [8]. While the objective of using Te(II) compounds as sacrificial electron donors for efficient H₂ generation was not achieved (only small amounts of H₂ were seen), the study led to the new compounds reported herein that have the first examples of Co(III)–Te(II) bonds.

2. Experimental section

2.1. Chemicals

Cobalt(II) chloride hexahydrate, cobalt(II) tetrafluoborate hexahydrate, cobalt(II) fluoride, dimethylglyoxime (dmgH₂), diphenylglyoxime (dpgH₂), are commercially available (Aldrich) and were used as received. Absolute ethanol and 96% ethanol were purchased from Fisher and used without further purification. The tellurium(II) ligands PhTe(CH₂)₃SO₃Na (L1) [9] and Te(anisyl)₂ (L2) [10] were synthesized as reported in the literature.

2.2. [Co(dmgH)₂{PhTe(CH₂)₃SO₃Na}₂]BF₄·2H₂O (1.BF₄)

To a solid mixture of 200 mg (0.57 mmol) of PhTe(CH₂)₃SO₃Na, 97 mg (0.285 mmol) of Co(BF₄)₂·6H₂O, 66.4 mg (0.57 mmol) of dimethylglyoxime and 24 mg (0.285 mmol) of NaHCO₃ was added 5 mL of water. Heating at 60 °C for 30 min led to the formation of a dark red solution. Filtration, concentration and addition of 15 ml of absolute ethanol afforded a red–brown solid that was washed with absolute ethanol (10 mL) and then with diethylether (10 mL) to yield 230 mg of product (66% yield). The compound exists as a 50–50 mixture of *meso* and *rac* diastereomers. For X-ray characterization, orange needles of the *meso* isomer were obtained on standing from hot saturated solutions of the compound in EtOH (99%)–H₂O (1%).

2.2.1. ¹H NMR of meso isomer

(400 MHz, D₂O, 25 °C): δ 1.76 (s, 6H, 2*Me*_a dmgH⁻), 1.96 (m, 4H TeCH_aH_bCH₂CH₂SO₃Na), 2.04 (s, 6H, 2*Me*_b dmgH⁻), 2.86 (m, 2H TeCH_aH_bCH₂CH₂SO₃Na), 2.87 (t, 4H, TeCH₂CH₂CH₂SO₃Na), 3.22 (m, 2H, TeCH_aH_bCH₂CH₂CO₃Na), 7.15 (m 4H, *o*-C₆H₅Te), 7.41 (m, 4H, *m*-C₆H₅Te), 7.58 (m, 2H, *p*-C₆H₅Te). ¹³C{¹H} NMR (100.6 MHz, D₂O, 25 °C): δ 12.26 (*C*_aH₃ dmgH⁻), 12.85 (*C*_bH₃ dmgH⁻), 14.74 (TeCH₂CH₂CO₃Na), 22.83 (TeCH₂CH₂CO₃Na), 51.11 (TeCH₂CH₂CH₂SO₃Na), 111.75 (*ipso*-TeC₆H₅), 130.58, 131.97, 134.09 (TeC₆H₅), 155.98 (MeC_a = N-dmgH⁻), 156.57 (MeC_b = NOH dmgH⁻).

2.2.2. ¹H NMR of rac isomer

(400 MHz, D₂O, 25° C): δ 1.90 (s, 12H, 4Me dmgH⁻), 1.96 (m, 4H TeCH_aH_bCH₂CH₂SO₃Na), 2.86 (m, 2H TeCH_aH_bCH₂CH₂SO₃Na), 2.87 (t, 4H, TeCH₂CH₂CH₂SO₃Na), 3.22 (m, 2H, TeCH_aH_bCH₂CH₂SO₃Na), 7.15 (m 4H, *o*-C₆H₅Te), 7.41 (m, 4H, *m*-C₆H₅Te), 7.58 (m, 2H, *p*-C₆H₅Te). ¹³C{¹H} NMR (100.6 MHz, D₂O, 25°C): δ 12.55 (CH₃ dmgH⁻), 14.74 (TeCH₂CH₂CH₂SO₃Na), 22.83 (TeCH₂CH₂CH₂SO₃Na), 51.11 (TeCH₂CH₂CH₂SO₃Na), 111.75 (*ipso*-TeC₆H₅), 130.58, 131.97, 134.09 (TeC₆H₅), 156.27 (MeC = NOH dmgH⁻).

¹²⁵Te NMR (500 MHz, D₂O, 25 °C): δ 712.3(s, 1Te), 713.3(s, 1Te). Under the same experimental conditions the ¹²⁵Te NMR of the free ligand PhTe(CH₂)₃SO₃Na (**L1**) showed one singlet at 449.1 ppm.

Anal. calc. for $C_{26}H_{40}BCoF_4N_4Na_2O_{12}S_2Te_2$: C, 28.09; H, 3.63; N, 5.04. Found: C, 28.26; H, 3.86; N, 4.63%.

UV–Vis (H₂O): λ_{max} = 425 nm ($\varepsilon \sim 26155 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)

2.3. [Co(dmgH)₂{PhTe(CH₂)₃SO₃Na}₂]F.3H₂O (1.F)

This compound was prepared following the same procedure as above for **1.BF**₄ but using CoF₂ instead of Co(BF₄)₂·6H₂O. Yield 65%. The compound is also a 50–50 mixture of *meso* and *rac* diastereomers. ¹H NMR and ¹³C{¹H} NMR spectra are identical to that described above for **1.BF**₄.

Anal. calc. for $C_{26}H_{42}CoFN_4Na_2O_{13}S_2Te_2$: C, 29.41; H, 3.99; N, 5.28. Found: C, 29.06; H, 3.85; N, 5.25%.

2.4. $[CoCl(dmgH)_2\{Te(p-MeO-C_6H_4)_2\}]$ (2)

To a solid mixture of 195 mg (0.57 mmol) of Te(*p*-MeO-C₆H₄)₂, 67.8 mg (0.285 mmol) of CoCl₂·6H₂O, 66.4 mg (0.57 mmol) of dimethylglyoxime and 24 mg (0.285 mmol) of NaHCO₃ was added 10 mL of absolute ethanol. Stirring in air for 24 h led to a red precipitate that was filtered and washed with 3 mL of absolute ethanol and then with 2 × 3 mL aliquots of diethylether. Yield 120 mg, 63%.

¹H NMR (400 MHz, CDCl₃, 25 °C): δ 2.20 (s, 12H, 4*Me* dmgH⁻), 3.86 (s, 6H MeO-C₆H₄), 6.94(d, 4H, MeO-C₆H₄), 7.39 (d, 4H, MeO-C₆H₄). ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C): δ 12.81 (CH₃ dmgH⁻), 55.47 (*MeO*-C₆H₄), 101.87, 115.81, 136.86, 152.47 (TeC₆ H₄OMe), 162.23 (MeC = NOH dmgH⁻).

Anal. calc. for $C_{22}H_{28}CICoN_4O_6Te$: C, 39.65; H, 4.23; N, 8.41. Found: C, 39.41; H, 3,98; N, 8.11%.

2.5. $[CoCl(dpgH)_2\{Te(p-MeO-C_6H_4)_2\}]$ (3)

To a mixture of 195 mg (0.57 mmol) of Te(*p*-MeO-C₆H₄)₂, 67.8 mg (0.285 mmol) of CoCl₂·6H₂O, 137 mg (0.57 mmol) of diphenylglyoxime and 24 mg (0.285 mmol) of NaHCO₃ was added 10 mL of ethanol. Heating at 60 °C with stirring for 30 min led to a brown crystalline solid that was filtered and washed with 2×3 mL aliquots of ethanol and 2×3 mL aliquots of diethyl ether. Yield 250 mg, 96%. Yellow–orange needles for X-ray characterization were obtained from dichloromethane solutions into which hexane diffused slowly.

¹H NMR (400 MHz, CDCl₃, 25 °C): δ 3.84 (s, 6H MeO-C₆H₄), 6.93(d, 4H, MeO-C₆H₄), 7.00 (d, 8H, C₆H₅), 7.28(m, 12H, C₆H₅) 7.62 (d, 4H, MeO-C₆H₄). ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C): δ 55.46 (*MeO*-C₆H₄), 101.50, 116.39, 137.17, 153.61 (TeC₆H₄OMe), 127.56, 129.31, 129.71, 129.83 (*Ph* dpgh⁻) 162.51 (PhC = NOH dpgH⁻).

Anal. calc. for $C_{42}H_{37}CICoN_4O_6Te$: C, 55.09; H, 4.07; N, 6.12. Found: C, 54.90; H, 3.85; N, 6.06%.

2.6. Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.1 MHz). ⁵⁹Co (I = 7/2, 100%), ¹²⁵Te (I = -1/2, 6.99%) were measured on a Bruker model Avance 500 NMR spectrometer operating at 500.13 MHz proton NMR frequency. The ⁵⁹Co NMR was measured at 118.67 MHz and the ¹²⁵Te NMR was measured at 157.79 MHz. For ¹²⁵Te the sweep width was 1624 ppm and about 16 K transients were accumulated. All NMR spectra were recorded at room temperature (296 K). The ¹²⁵Te NMR chemical shifts are referenced with Te₂Ph₂ in toluene-d₈ as an external reference at 418.0 ppm [11]. All ⁵⁹Co NMR chemical shifts are reported with aqueous K₃[Co(CN)₆] sample as an external reference at 0.0 ppm [12].

2.7. Electrochemistry

Cyclic voltammetry experiments were conducted on an EG&G PAR 263A potentiostat/galvanostat using a three-electrode singlecompartment cell including a glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag wire pseudo-reference electrode. For all measurements, samples were degassed by purging with argon. Tetrabutylammonium hexafluorophosphate (Fluka) was used as the supporting electrolyte (0.1 M), and ferrocene was employed as an internal reference. All redox potentials were measured relative to the ferrocenium/ferrocene (Fc+/Fc) couple (0.40 V vs SCE) [13] that was used as an internal standard and then adjusted to NHE assuming an SCE potential of 0.24 V. All scans were performed at 100 mV s⁻¹.

2.8. X-ray structural determination of complexes $1.BF_4$, **3** and $[Co(dmgH)_2(py)_2]-[CoCl_2(dmgH)_2]$

Orange needles of [*meso*-**1**.BF₄·3EtOH], yellow-orange needles of **3** and orange needles of [Co(dmgH)₂(py)₂][CoCl₂(dmgH)₂] suitable for single crystal X-ray diffraction were maintained at 100.0(1) K, on a Bruker SMART platform diffractometer equipped with an APEX II CCD detector. The X-ray source, powered at 50 kV and 30 mA, provided Mo K α radiation (λ = 0.71073 A°, graphite monochromator). Space groups were determined based on systematic absences, intensity statistics, and space group frequencies. Direct methods were used to solve the structures [14]. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were given riding models and refined with relative isotropic displacement parameters.

3. Computational details

Density functional theory (DFT) calculations were carried out using Gaussian 03 (GAUSSIAN, Inc.) [15]. Time-dependent (TD) calculations were performed on the optimized ground-state structures in gas phase. All calculations employed the B3LYP [16] functional using the 6-31G(d,p) basis set for H, C, N and O, while Co and Te were approximated using LANL2DZ effective core potentials [17].

4. Results and discussion

When studying the reactivity of diaryltelluroethers Ar_2Te (Ar = Ph, 4-MeO–Ph, 4-NH₂–Ph) with solid [Co(dmgH)₂(py)Cl] in dry organic solvents such as dichloromethane or acetone, no reaction was observed. However, after the addition of water, these mixtures developed intense red colors. Despite the absence of well characterized examples of Co(III)–tellurium compounds, we presumed that the deep color was due to cobalt(III)–tellurium bonded species. Unfortunately, initial attempts to isolate these deeply colored compounds failed. Only crystals of known compounds like

[NBu₄][Co(dmgH)₂Cl₂], TeCl₂(4-MeO-Ph) [18] and [Co(dmgH)₂(-py)Cl] [19], as well as the not yet reported [Co(dmgH)₂py₂][-Co(dmgH)₂Cl₂], were obtained. In recognition of the fact that the intense red species formed only in protic solvents, a water soluble telluroether, PhTe(CH₂)₃SO₃Na, was employed for additional synthesis [9].

Treatment of aqueous cobalt(II) salts with PhTe(CH₂)₃SO₃Na in the presence of dimethylglyoxime and sodium bicarbonate in aerobic conditions afforded highly colored solutions of the complex [Co(dmgH)₂{PhTe(CH₂)₃SO₃Na}₂]⁺ (**1**⁺). However, attempts to prepare the neutral *mono*-tellurium substituted complex [CoCl (dmgH)₂{PhTe(CH₂)₃SO₃Na}] proved unsuccessful in yielding a pure product. On the other hand, analogous reactions with Te(*p*-anisyl)₂ that were carried out in absolute ethanol, did indeed lead to the neutral *mono*-tellurium complexes [CoCl(dmgH)₂ {Te(*p*-MeO-C₆H₄)₂}] (**2**) and [CoCl(dpgH)₂{Te(*p*-MeO-C₆H₄)₂}] (**3**). The different results of the reactions for the two different Te ether compounds appear to correlate with solvent polarity with the more polar aqueous medium favoring the cationic bis telluroether complexes, and the less polar EtOH affordiing the neutral mono telluroether product.

4.1. Structural characterization in solution

4.1.1. ¹H and ¹³C NMR

The ¹H NMR spectrum of complex $1.8F_4$ in D_2O is shown in Fig. 1. The methyl groups of the dmgH ligands appear as three singlets in a 1:2:1 ratio at δ 1.76 1.90 and 2.04 ppm. To understand the nature of these resonances, it is necessary to consider that coordination of **L1** through tellurium leads to chirality as shown in Scheme 1 and that for a Te center having three different groups bonded to it, pyramidal inversion is extremely slow on the NMR timescale. Note that as a consequence of the chirality, the protons of the methylene bonded to Te are diasterotopic.

The synthesis and stereochemistry of optically active tricoordinate tellurium compounds, such as telluroxides, telluronium salts and telluronium ylides were reviewed in 1997 (see Scheme 2) [20]. Configurationally stable telluroxides were only obtained with bulky groups, but the mechanism for racemization in the presence of water were thought to involve an achiral hydrate rather than simple pyramidal inversion at Te. The pyramidal inversion energy for Me₂TeO was estimated to be about 64 kcal mol⁻¹ based on an *ab initio* MO study. Enantiomerically pure (R)-telluronium salts [MeEtPhTe]X (X = BF₄⁻⁷, ClO₄⁻⁷) were found to be stable toward pyramidal inversion, with no racemization taking place even after refluxing in methanol for 3 days [20].

In the present study, coordination of two chiral ligands in the trans axial positions of the octahedral $[Co^{III}L_2(dmgH)_2]^+$ complex



Fig. 1. ¹H NMR spectrum of **1.BF₄**. Signal due to residual H₂O at 4.72 ppm has been removed for clarity.



Fig. 2. The R, S or *meso*-isomer of the cation $\{Co^{III}(dmgH)_2[PhTe(CH_2)_3SO_3Na]_2\}^*$ which has point symmetry C_{2h} and is therefore achiral. This meso isomer has two chemically inequivalent methyl groups.



Fig. 3. The S,S enantiomer of the cation rac-[Co^{III}(dmgH)₂{PhTe(CH₂)₃SO₃Na}₂]⁺⁻ which has point symmetry D₂ with all dmgH methyl groups equivalent.

leads to diastereomers as shown in Figs. 2 and 3. This consists of a 50% achiral meso isomer and a 50% chiral *rac* isomer. The *rac* isomer is 25% S-S and 25% R–R. In the *meso* isomer, there is a mirror plane coincident with the $Co^{III}(dmgH)_2$ moiety but the methyl groups on each dmgH ligand remain distinct, Me_a and Me_b. There

is no symmetry element that interchanges these two methyl groups on each dmgH. However, in the case of the *rac* isomer, a C_2 axis yields equivalence of the methyl groups (see Scheme 3 where A, B, C denotes different substituents on tellurium), leading to only one Me resonance (the symmetry of the meso diastereomer ignoring the methyl protons is C_{2h}).

Hence, the central signal of the three Me singlets at 1.90 ppm (that belongs to the *rac*-diastereomer) integrates to exactly double the value of the two signals at 1.76 and 2.04 ppm (that belong to the *meso*-diastereomer). The same explanation applies to what is observed in the ¹³C NMR spectrum. The explanation indicates that both meso- and rac-isomers are in equal amounts, indicating that the reaction yields a purely statistical result. There is no preference for binding of a prochiral ligand to the Co center for which the trans ligand has a specific chirality. The diastereotopic methylene group attached directly to Te shows separate $-CH_2$ - signals at 3.22 ppm and 2.86 ppm, the latter overlapping with the signal of the methylene directly attached to the sulfonate S atom.

These stereochemical results are in agreement with the reported presence of meso and dl diastereomers in square planar complexes [MX₂{PhTe(CH₂)₃TePh}] (M = Pd, Pt; X = Cl, Cr, I) and in ruthenium(II) complexes that were properly established by NMR spectroscopy [8]. Nevertheless, the discussion about the stereochemistry in systems containing coordinated asymmetric telluroethers has often been overlooked. For instance, the coordination chemistry of the arylalkyltellurium ligand 2-[2-(4-methoxyphenyltelluro)ethyl]thiophene has been reported but neither the expected chiral nature of the ligand after coordination nor its influence on the ¹H NMR spectrum (i.e., the diastereotopic nature of the methylene group attached to tellurium) was mentioned [21]. The same applies to the 4-MeOC₆H₄TeCH₂CH₂SEt (L) and its complex [PdCl₂L] whose structure, with both Te and S having three different substituents plus the lone pair, was published, but with no mention of its stereochemistry [22]. Likewise, the complex [Pd{4-MeC₆H₄TeCH₂CH₂-2-(C₅H₄N)}Cl₂] was structurally characterized, but no stereochemical discussion was included [23].

4.1.2. ¹²⁵Te NMR spectroscopy

The ¹²⁵Te NMR of **1**.BF₄ in D₂O was readily observed and the spectrum show two resonances at 713.4 and 712.3 ppm as expected from the presence of two diastereomers. The ¹²⁵Te NMR lines are considerably broader compared to the ca. 1.5 Hz linewidth of the reference peak of Te₂Ph₂. In many tellurium compounds, ¹²⁵Te often shows spin-spin couplings to other nuclei such as proton, carbon and phosphorus [24]. We were therefore interested in the observation of its one-bond spin-spin coupling (¹J_{Co-Te}) to the ⁵⁹Co (*I* = 7/2) nucleus present in 100% natural abundance. However, due to the rapid quadrupolar relaxation of the ⁵⁹Co nucleus, we were unable to observe any spin-spin coupling of ¹²⁵Te to the cobalt nucleus in all the complexes studied here. Additionally, the large linewidths of the ¹²⁵Te resonances of the



Scheme 3.



Fig. 4. Perspective view of complex $1.BF_4$ with atomic numbering scheme. All hydrogen atoms have been omitted for clarity.

complexes examined here relative to the reference sample of Te₂Ph₂ indicate that those resonances are affected substantially by quadrupolar interaction with the ⁵⁹Co nucleus.

Although ⁵⁹Co has reasonably high sensitivity and cobalt(III) NMR spectra are readily measured for most cobalt complexes with high symmetry such as the octahedral $K_3[Co(CN)_6]$, the cobalt NMR resonances are exceedingly broad and sometimes difficult to observe for unsymmetrical complexes [25]. In fact, the large



Fig. 6. ORTEP diagrams of complex [Co(dmgH)₂(py)₂][CoCl₂(dmgH)₂] with atomic numbering scheme.

electric field gradient and efficient quadrupolar relaxation in complexes **1–3** cause the ⁵⁹Co NMR peaks to broaden beyond detection



Fig. 5. Perspective view of complex 3 with atomic numbering scheme. All hydrogen atoms have been omitted for clarity.

by 59 Co NMR spectroscopy and we were, therefore, unable to observe 59 Co resonances from the complexes containing tellurium directly bonded to Co(III).

4.2. Structural characterization in solid

The solid-state molecular structures of the title cobalt-tellurium compounds *meso*-**1**.BF₄·3EtOIH and **3**, as well as the ionization isomer $[Co(dmgH)_2(py)_2][CoCl_2(dmgH)_2]$ of $[CoCl(dmgH)_2(py)]$, were determined by single-crystal X-ray crystallography. The structures of these complexes are shown in Figs. 4–6 with important crystallographic parameters in Table 1. All of the structures contain octahedrally coordinated Co(III) with a planar Co(glyoximate)₂ moiety and *trans* axial ligands.

The asymmetric unit of the cationic complex *meso*-**1**.BF₄·3EtOH contains two half-molecules of the complex in which the Co(III) ion in each is located on a crystallographic inversion center. The asymmetric unit also contains three independent Na⁺ ions, two which are in crystallographic inversion centers and one in a general position, one tetrafluoroborate anion, and four ethanol solvent molecules, two in general positions and two disordered on crystallographic inversion centers. The neutral complex **3** shows two coplanar diphenylglyoximate ligands and trans chloride and Te(p-anisyl)₂ ligands. The cobalt(III)-tellurium distances are 2.5872(11) Å and 2.5617(10) in complex **1**.BF₄ and 2.5252(5) Å in complex **3** and, although there are no previously reported X-ray characterized Co(III)–Te complexes, they compare very well with the distance 2.561 Å found in TePh₂ bonded to cobalt in a carbonyl cluster [26]. In complex 1.BF₄, the average Co–N bond distance was found to be 1.884 Å with a corresponding chelate angle of 81.4°.

Complex **3** has Co–N bonds with an average distance of 1.886 Å with a corresponding chelate angle of 81.23°. For a more detailed description of bond length and angles, please see the CIF files included in Supporting Information.

For the ionization isomer $[Co(dmgH)_2(py)_2][CoCl_2(dmgH)_2]$, the separate structures of the cation $[Co(dmgH)_2(py)_2]^+$ and anion $[CoCl_2(dmgH)_2]^-$ had been reported previously [27], and the bond lengths and angles found here are consistent with those reported for the respective cationic and anionic cobalt(III) bis(dimethylglyoximate) complexes. The metrical parameters for this structure are provided in the Supporting Information in CIF format.

4.3. Electronic absorption and DFT calculations

The origin of the intense color of complex 1^+ , due to a low-energy band centered at 425 nm ($\varepsilon \sim 26155 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, half bandwidth $\sim 50 \text{ nm}$) merits some attention as complexes of the type [Co(dmgH)₂LCI], where L is a N or P donor ligand only exhibit strongly absorbing bands with ε on the order of $10^4 \text{ dm}^3 \text{ mol}^{-1} - \text{cm}^{-1}$ at wavelengths below 300 nm, corresponding to spin allowed intraligand ($\pi - \pi^*$) transitions [4a]. Such intense transitions had not been noted for reported complexes containing Co–Te bonds [28]. The observed coloration of the title complexes results from important changes in the axial metal–ligand interactions that are similar to the differences seen when going from Ru–Cl to Ru–Sn bonds as observed in the electronic structure of d⁶ metal-diimine complexes [RuCl(Me)(CO)₂(ⁱPr-DAB)] and [Ru(SnPh_3)(Me)(CO)₂(ⁱPr-DAB)] [29].

In order to shed light on the origin this low energy band theoretical TD DFT calculations were performed using X-ray

Table 1

Crystal data and structure refinement for complexes *meso*-1.BF₄·3EtOH, 3 and [Co(dmgH)₂(py)₂][CoCl₂(dmgH)₂].

Identification code	meso-1.BF ₄ ·3EtOH	3	$[Co(dmgH)_2(py)_2][CoCl_2(dmgH)_2]$
Empirical formula	C32 H54 B Co F4 N4 Na2 O13 S2 Te2	C42 H36 Cl Co N4 O6 Te	C26 H38 Cl2 Co2 N10 O8
Formula weight	1213.83	914.73	807.42
T (K)	100.0(1)	173.0(5)	100.0(1)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	P2/n	PĪ	C2/c
Unit cell dimensions			
a (Å)	13.610(6)	10.7835(10)	26.684(3)
$b(\hat{A})$	11.214(5)	2.0447(11)	7.8859(9)
c (Å)	29.219(13)	16.5094(15)	15.8520(19)
α (°)	90°	104.029(2)	90
β (°)	97.514(5)	106.321(2)	93.692(3)
γ (°)	90	94.938(2)	90
$V(Å^3)$	4421(3)	1968.9(3)	3328.8(7)
Z	4	2	4
Density (calculated) (Mg/m ³)	1.824	1.543	1.611
Absorption coefficient (mm ⁻¹)	1.876	1.283	1.220
F (000)	2416	920	1664
Crystal color, morphology	orange, needle	yellow-orange, needle	orange, needle
Crystal size (mm)	0.24 imes 0.16 imes 0.12	0.24 imes 0.12 imes 0.08	0.28 imes 0.14 imes 0.06
θ (°)	1.58-28.28	1.77-29.57	2.58-37.03
Index ranges	$-18 \leq h \leq 17, 0 \leq k \leq 14, 0 \leq l \leq 38$	$-14 \leq h \leq 14, -16 \leq k \leq 16,$	$-44 \leq h \leq 44, -11 \leq k \leq 13,$
-		$-22 \leq l \leq 22$	$-26 \leqslant l \leqslant 22$
Reflections collected	108737	33 520	23808
Independent reflections (R_{int})	10915 (0.0856)	11029 (0.0600)	8437 (0.0789)
Observed reflections	9556	7280	4674
Completeness to theta = 29.57°	99.1%	99.9%	99.4%
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.8062 and 0.6616	0.9043 and 0.7483	0.9304 and 0.7263
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10915/9/608	11029/0/498	8437/16/291
Goodness-of-fit (GOF) on F^2	1.170	1.024	0.968
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0526$, $wR_2 = 0.1193$	$R_1 = 0.0492, wR2 = 0.0953$	$R_1 = 0.0521, wR_2 = 0.1021$
R indices (all data)	$R_1 = 0.0634, wR_2 = 0.1221$	$R_1 = 0.0844, wR_2 = 0.1116$	$R_1 = 0.1154, wR_2 = 0.1249$
Largest difference in peak and hole	1.677 and -1.543	0.638 and -0.712	0.961 and -0.635
(e Å ⁻³)			

experimental data of compound $\mathbf{1}^+$, where substituents on tellurium atoms were simplified to methyl groups. The calculated highest value of oscillator strength found is 0.0076 with a transition energy (singlet) of 457 nm which correspond to the transition LU-MO \leftarrow HOMO-2. HOMO-2 has π^* N–O character and it is situated on the coordination plane of glyoximate ligands (see figures in Supplementary Material). The LUMO is mainly composed of p atomic orbitals of tellurium and a *d* orbital of cobalt resulting in σ^* character. A similar electronic structure with slight differences in the order of the energy levels has been reported for the d^6 octahedral complex [Pt(SnH₃)₂(CH₃)₂(ⁱPr-DAB)] [30]. In short, the intense color of complex $\mathbf{1}^{+}$ may be assigned to a ligand (π^{*} dmgH centered) to metal (σ^* Te–Co–Te centered) charge transfer LMCT transition.

4.4. Hydrogen production experiments

These unique cobaloxime-tellurium complexes were tested as potential catalysts under the published experimental conditions [5c]. When paired with multiple chromophores $(Ru(bpy)_3^{2+}, Eosin$ Y, and Fluorescein) and irradiated with visible light ($\lambda > 400 \text{ nm}$) hydrogen was produced. However, the activity was very weak (TON < 3) under these reaction conditions. Various solvent mixtures and sacrificial donors were also examined but hydrogen generation was still modest. To test if the telluroethers act as intramolecular electron donors in these systems, we performed the same photocatalytic experiment without the addition of excess sacrificial donor. Unfortunately, in these studies no hydrogen generation was detected by GC.

4.5. Electrochemistry

Cyclic voltammetry studies were performed on complexes in MeCN with 0.1 M tetra-n-butylammonium hexfluorophosphate as the supporting electrolyte under an argon atmosphere. Complex 1.BF₄ exhibited an irreversible oxidation wave at 1.33 V and a reversible reduction wave at 0.01 V. A reversible reduction wave was also observed at -0.56 V. Similarly, complex 2 exhibits an irreversible oxidation at 1.30 V, an irreversible reduction at -0.15 V, and a reversible reduction at -0.81 V. Complex 3 exhibits an irreversible oxidation at 1.10 V, an irreversible reduction at 0.05 V, and a reversible reduction at -0.55 V. All of the redox potentials were measured and adjusted to NHE using the ferrocenium/ferrocene (Fc⁺/Fc) couple as an internal standard and then adjusting the potentials using literature values for the internal standard (0.40 V vs SCE, SCE vs NHE = 0.24 V) [13].

5. Conclusion

The first examples of Co(III) complexes with diorganotellurides have been prepared and fully characterized. The previous absence of structurally characterized compounds containing Co(III)-Te bonds has been overcome through the bonding of Te to the axial positions of cobalt bis-glyoxime complexes. Three singlets were also observed in the ¹H NMR spectra corresponding to R,S and S,S meso-isomers of complex 1. In contrast with classical HSAB theory, we report the binding of a soft base (Te) to a hard acid (Co^{III}).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version. at http://dx.doi.org/10.1016/i.polv.2012.08.017.

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