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A Convergent Approach to the Synthesis of Multimetallic Dithiolene Complexes

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Controlled base hydrolysis of one or both of the protected 1,2-dithiolene chelates of 1,3,5,7-tetrathia-*s*-indacene-2,6-dione ($O{=}CS_2C_6H_2S_2C{=}O$) enables the stepwise synthesis of di- and trimetallic complexes with 1,2,4,5-benzenetetrathiolate as the connector. Treatment of $O{=}CS_2C_6H_2S_2C{=}O$ with MeO^-, followed by $[NiBr_2(dcpe)]$ [dcpe = 1,2-bis(dicyclohexylphosphino)ethane], yields $[(dcpe)Ni(S_2C_6H_2S_2C{=}O)]$ (**4**). The reaction of **4** with EtO^-, followed by $[MX_2(dcpe)]$ (X = halide), yields $[(dcpe)Ni(S_2C_6H_2S_2)M(dcpe)]$ [M = Ni (**5a**), Pd (**5b**)]. Deprotection of the 1,3-dithiol-2-one group of **4**, followed by introduction of $^1/_2$ equiv of MX_2 and then I_2, yields the neutral trimetallic compounds $[(dcpe)Ni(S_2C_6H_2S_2)]_2M$ [M = Ni (**6a**), Pt (**6b**)]. Tetrahedralization at nickel is observed in **5a**, which density functional theory calculations attribute to second-order Jahn−Teller effects, while **6a** and **6b** display an end-to-end folding of ~46°. A color darkening is observed in moving from **4** to compounds **6** due to the increasing size of the conjugated metal−organic π system. Intense, broad absorptions in the near-IR are observed for **6a** and **6b**.

The rich photophysical and redox behavior associated with metal dithiolene complexes has stimulated a considerable body of research into their possible application as conducting materials,[1] molecular magnets,[1] sensing devices,[2] and chromophores in photocatalytic systems.[3] The vast majority of this work has focused upon monometallic systems. More recently, some effort has been directed at the synthesis of dimetallic dithiolene complexes with the idea that the properties that have elicited so much attention in monometallic systems may be enhanced, or perhaps to some degree tailored, in a metallodithiolene complex containing two or more metal atoms. Noteworthy examples of dimetal complexes with bis(dithiolene)-type bridging ligands include $[Cp_2M]_2(S_2C_6H_2S_2)$ (M = Ti, Zr, Hf),[4] $[L_2M]_2(\mathrm{ttft})$ (L = Cp, Cp*, M = Ti; L = Ph_3P, M = Pt)[5,6] $[[Ni(S_2C_2S_2C_2(CO_2Me)_2)]_2(\mathrm{tto})]^n$ (n = 0, 2),[6,7] $(Bu_4N)_2[[Ni(\mathrm{dmit})]_2(\mathrm{tto})]$,[8] $[[(\mathrm{edo})Ni]_2(\mathrm{tto})]^{2-}$ [6,9] and $[Cp^*Co(S_2C_6H_2S_2)CoCp^*]$.[10] In two instances, trinickel species have been isolated and characterized,[9] albeit in low yield and as one component in a mixture. A hindrance to the further pursuit of these interesting types of compounds has been the absence of more deliberate methods of synthesis that circumvent the formation of insoluble metallodithiolene polymer and that are amenable to a generalized preparative approach for a broad variety of multimetal dithiolene molecules. One suggestion of such an approach appeared in work by Purrington, Bereman, and coworkers,[11] who described the stepwise base hydrolysis of 4,4′-bis(1,3-dithiol-2-one) and the synthesis of dimetallic complexes, including heterodimetallic complexes, joined by the butadienetetrathiolate ligand. Described herein is a controlled deprotection of a doubly protected bis(dithiolene) ligand for the facile synthesis of di- and trimetallic dithiolene bis(phosphine) complexes using 1,2,4,5-benzenetetrathiolate as a bridging bis(dithiolene) ligand.

Scheme 1 summarizes the syntheses reported here of new di- and trimetallic complexes using 1,2,4,5-benzenetetrathi-

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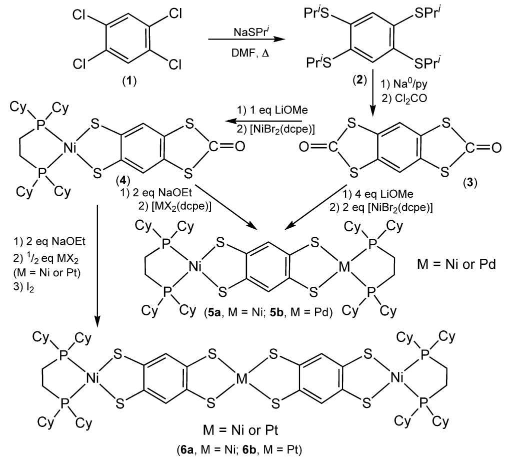
Scheme 1. Synthesis of Di- and Trimetallic Complexes with 1,2,4,5-Benzenetetrathiolate as a Bridging Bis(dithiolene) Ligand (Cy = cyclohexyl; X = Halide)



olate as a connecting ligand. Of the various preparations for protected forms of 1,2,4,5-benzenetetrathiol that have been described, the method of Bechgaard for the preparation of 1,3,5,7-tetrathia-*s*-indacene-2,6-dione (**3**) is the most convenient and cost-effective.[12] By a route beginning with tetrachlorobenzene and proceeding through 1,2,4,5-tetrakis(2-propylthio)benzene (**2**), multigram quantities of 1,3,5,7-tetrathia-*s*-indacene-2,6-dione (**3**) are conveniently obtained. The 1,3-dithiol-2-one moieties in this molecule are readily unmasked by base hydrolysis to liberate one or both of the arene-1,2-dithiolate chelates. The virtue of this controlled, stepwise base hydrolysis of the protected benzenetetrathiolate is the ability to avoid the formation of an insoluble metal dithiolene polymer and instead to prepare well-defined metal dithiolene complexes of increasing complexity through a convergent-type synthesis.

The addition of 1 equiv of MeO^- to a suspension of **3** in 1:1 MeOH/THF, followed by the addition of [$NiBr_2$(dcpe)],[6] enables the formation of the orange mononickel compound [Ni(dcpe)($S_2C_6H_2S_2C{=}O$)] (**4**) in 62% yield. Here, the use of a substoichiometric 1 equiv of MeO^- optimizes the monodeprotection of **3** relative to double deprotection. The use of 4 equiv of MeO^- in THF/MeOH leads to full deprotection of **3** and, following the addition of 2 equiv of [$NiBr_2$(dcpe)], to red-brown dinickel compound **5a** in 65% yield. Alternatively, **5a** can be prepared in 47% yield from isolated **4**, which is treated with 2 equiv of EtO^- in THF/MeOH and then reacted with [$NiBr_2$(dcpe)]. This ability to hydrolyze the peripheral 1,3-dithiol-2-one group in **4** without an adverse effect upon the remainder of the molecule allows the opportunity to synthesize heterodimetallic compounds, e.g., the mixed nickel−palladium compound **5b**, by introduction of [$PdCl_2$(dcpe)] to deprotected **4**. The mixed-metal composition of **5b** has been confirmed, inter alia, by MALDI mass spectrometry. Viewing **4** as a protected metallodithiolene "ligand" poses the idea of using 2 or 3 deprotected equiv thereof to synthesize new, elaborated types of multimetallic bis- and tris(dithiolene) complexes. Thus, the mixing of 2 equiv of deprotected **4** with 1 equiv of $NiCl_2 \cdot 6H_2O$ or of $PtCl_2$, followed by the addition of I_2 to oxidize the resulting dianion, produces charge-neutral trinickel compound **6a** or the mixed nickel−platinum species **6b**. These products are formed in moderate yields, are readily prepared in highly crystalline form, and are amenable to characterization by a variety of physical methods.

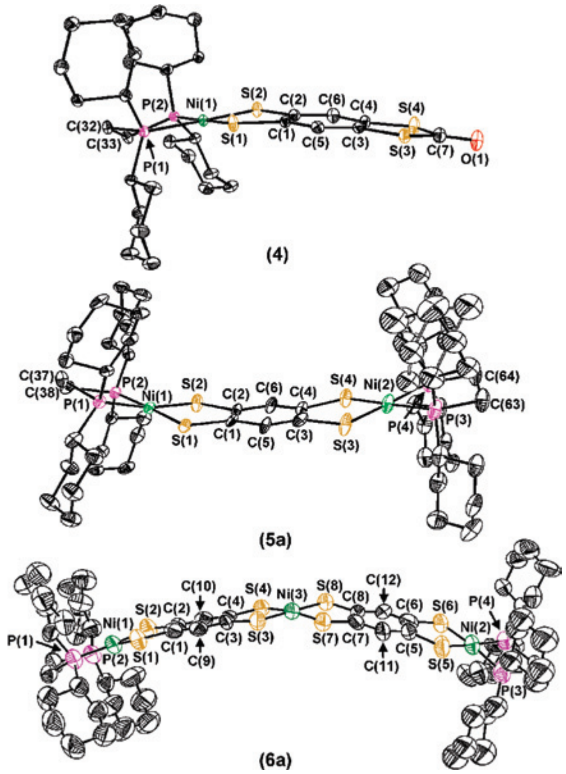


Figure 1. Thermal ellipsoid plots of [(dcpe)Ni($S_2C_6H_2S_2C{=}O$)] (**4**; 50%), [(dcpe)Ni]$_2$($S_2C_6H_2S_2$) (**5a**; 50%), and [[(dcpe)Ni($S_2C_6H_2S_2$)]$_2$Ni] (**6a**; 40%). H atoms are omitted for clarity.

The new compounds shown in Scheme 1 have all been authenticated by X-ray crystallography (Figure 1). The structure of **4** reveals nearly square-planar coordination geometry about nickel and a slight degree of bending of the arene unit relative to the P_2NiS_2 mean plane. Compound **5a** shows more a pronounced deviation from planarity, with both nickel centers tetrahedrally distorted and both P_2NiS_2 mean planes folded toward the same side of the arene ring (Figure 1). The angle between the two P_2NiS_2 mean planes is 26°, while the mean deviations from the P(1)−P(2)−Ni(1)−S(1)−S(2) and P(3)−P(4)−Ni(2)−S(3)−S(4) best-fit planes are 0.114 and 0.025 Å, respectively. In contrast, the mean deviation from the P(1)−P(2)−Ni(1)−S(1)−S(2) plane in **4** is only 0.012 Å.

Two molecules of **5a** occur in the asymmetric unit of the unit cell in noncentric space group *Pc* and reside on general positions. Both independent molecules reveal a similar type and degree of nonplanarity, which suggests that this structural feature is not incidental but rather indicative of specific symmetry interactions within the electronic structure. The heterodimetallic nickel−palladium compound **5b** crystallizes in the centric space group $P\bar{1}$ with Ni and Pd atoms statically disordered. The optimal site occupancy description for the Ni atom over the two metal atom positions is a 40:60 distribution. Distortions that are qualitatively similar to those

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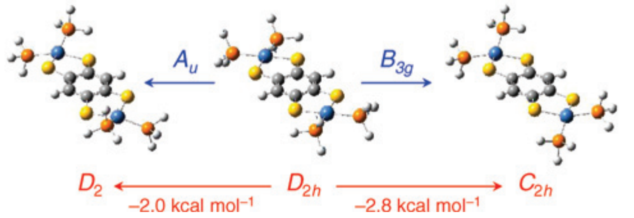

Figure 2. Optimized D_2, D_{2h}, and C_{2h} structures of **5a′** and their energies relative to the D_{2h} structure. Negative numbers indicate stabilization. Only the D_2 and C_{2h} geometries are potential energy minima.

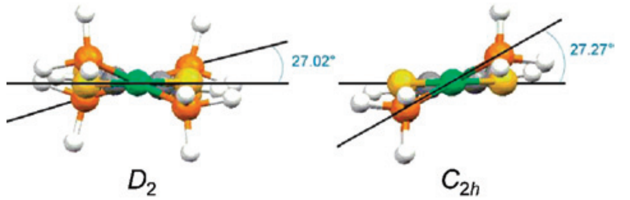

Figure 3. View of **5a′** along the Ni−Ni axis in both the D_2 and C_{2h} point groups. For both geometries, the central NiS_4Ni unit is essentially planar. In D_2, the two P_2Ni planes are staggered at 54.04° relative to each other and at 27.02° in opposite directions relative to the central NiS_4Ni plane. In C_{2h}, the two P_2Ni planes are coincident and form a dihedral angle of 27.27° with the NiS_4Ni plane.

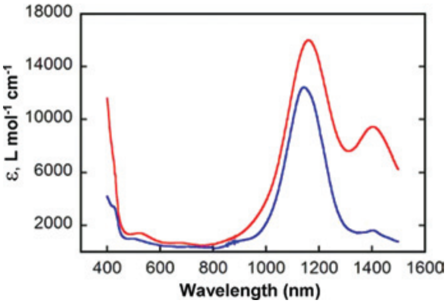

Figure 4. UV−vis and near-IR spectra in an *N*,*N*-dimethylformamide solution of $[(dcpe)Ni(S_2C_6H_2S_2)M(S_2C_6H_2S_2)Ni(dcpe)]$ (M = Ni, red; M = Pt, blue).

in **5a** are observed in **5b**, which lends further credence to the possibility that these structural properties may be attributable to more than crystal-packing effects.

Compounds **6a** and **6b** both crystallize in rhombohedral space group $R\bar{3}$ and reveal still greater bending from end to end, with the angle between the terminal P_2NiS_2 mean planes being 46°. The twisting in **6a**, distinct from the bending, is 21° clockwise as determined by the torsion angle defined by the P(1)−Ni(1) bond, the Ni(1)−Ni(2) interatomic vector, and the Ni(2)−P(3) bond. Structurally, **6b** is highly similar to **6a**, with bending and twisting angles of 47° and 24°, respectively. It is likely that, if stereoelectronic effects are indeed governing the structure of **5a** and **5b**, they are pertinent to molecules **6a** and **6b** as well.

Density functional theory calculations[13] were undertaken to rationalize the distorted tetrahedral geometry about nickel in **5a**. A model complex **5a′** was chosen where H atoms replace the alkyl substituents on phosphorus. A geometry optimization within full D_{2h} symmetry converged to an unstable structure having two imaginary vibrational frequencies, of A_u and B_{3g} symmetry (Figure 2). Deformation along the A_u mode leads to a D_2 structure and that along the B_{3g} mode to a C_{2h} geometry; both are energy minima by harmonic frequency calculations. Figure 3 offers an alternative presentation of the D_2 and C_{2h} structures for further emphasis of their differences. The C_{2h} isomer is the lowest-energy structure, being 0.038 eV (0.88 kcal mol^{-1}) more stable than the D_2 geometry and 0.12 eV (2.8 kcal mol^{-1}) more stable than the idealized D_{2h} complex. The distortions to lower symmetry result from configuration interaction (CI). The highest occupied Kohn−Sham orbital (HOMO) in D_{2h} symmetry is b_{2g}, and the lowest unoccupied orbital (LUMO) is b_{2u}. In D_2 symmetry, these both become b_2 and CI between them stabilizes a D_2 structure over D_{2h}. The LUMO + 1 in D_{2h} symmetry is b_{1g}; in C_{2h}, it and the HOMO both become b_g, and they engage in CI. A structure (C_{2h}) of lower symmetry than D_{2h} results. Both the D_2 and C_{2h} distortions cause "tetrahedralization" at nickel and are instances of the second-order Jahn−Teller instability.[14] The bending distortion observed in **5a**, which is distinct from the tetrahedralization at the metal atoms, has not been reproduced in the calculations and may require a model compound that more accurately simulates the basic nature and structural constraints of the dcpe ligand.

One obvious change in proceeding from compound **4** to molecules **5** and then **6** is a progressive darkening in color from orange to red-brown to brown-black. This color change is expected as the conjugated π system is made more extensive. The most prominent feature of the UV−vis−near-IR spectra of molecules **6** (Figure 4) is the relatively intense, low-energy absorption in the near-IR at 1159 and ∼1408 nm for **6a** and at 1177 nm for **6b**. It is possible that these electronic absorptions are due to interligand intervalence charge-transfer transitions involving fully reduced ene-1,2-dithiolates and partially oxidized thienyl radical monoanions.

In summary, the present work describes an approach to the synthesis of multimetal dithiolene complexes based upon the selective monodeprotection of 1,3,5,7-*s*-indacene-2,6-dione, which is a doubly protected form of 1,2,4,5-benzenetetrathiolate. It is probable that the synthetic approach by which molecules **6a** and **6b** have been prepared can be extended to the synthesis of "linear" pentametallic molecules. The flexibility inherent to this method of synthesis may permit the preparation of metallodithiolene compounds, including heterometallic compounds, whose physical properties can be tailored with a very high degree of control.

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Supporting Information Available: Full crystallographic data in CIF format and preparative procedures, computational details, and Cartesian coordinates of optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Full details appear in the Supporting Information.

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