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Charge-Transfer Complexes

Trapping of a Thiolate→Dibromine Charge-Transfer Adduct by a Macrocyclic Dinickel Complex and Its Conversion into an Arenesulfenyl Bromide Derivative**

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A large number of charge-transfer (CT) or electron donor–acceptor complexes of the halogens have been reported and their characterization has significantly contributed to our understanding of chemical bonding.[1] Whereas halogen adducts of regular electron-pair donors, such as alcohols, ethers, thioethers, and thiones are quite common,[2–4] stable CT complexes incorporating the extremely good thiolate donors have been described far less frequently. The parent thiolate dihalogen adducts ($RS^-\rightarrow X_2$, X = Br, I) have been invoked as first intermediates in the reaction between thiolates and dihalogens that results in the formation of sulfenylhalides RSX and disulfides RSSR,[5] but have never been isolated in their free forms. In a few cases, however, such species have been stabilized in the coordination sphere of transition-metal thiolate complexes. Thus, only a handful of diiodine adducts of metal thiolate complexes have been isolated[6] and thiolate→Br_2 CT complexes are unknown. Herein, we report the synthesis and characterization of a unique dibromine CT adduct of a macrocyclic nickel(II) amine thiophenolate complex and its conversion into an arenesulfenyl bromide complex.

The reaction of $[Ni_2L(OAc)][ClO_4]$ (**1**)[7] with one equivalent of dibromine in CH_3CN at 0 °C leads to the immediate formation of a dark brown solution, from which black lustrous crystals, characterized as the paramagnetic Br_2 adduct $[Ni_2L(OAc)\cdot Br_2][ClO_4]$ (**2**), are obtained in 70 % yield (Scheme 1). Carrying out the reaction in propionitrile gave single crystals of **2**·CH_3CH_2CN suitable for a single-crystal X-ray structure analysis.[8]

The structure of **2**·CH_3CH_2CN revealed the presence of well-separated complex cations (Figure 1), ClO_4^- ions, and solvate molecules.[8] The linear RS-Br-Br arrangement (S-Br-Br 178.51(3)°), the significant lengthening of the Br–Br bond to 2.6980(7) Å (compared to 2.27 in free Br_2[1]), and a S–Br distance of 2.401(1) Å, respectively, confirm the CT nature of this complex. The S–Br distance is significantly longer than the value of approximately 2.18 Å predicted for a covalent S–Br single bond[9] and is within the range of S–Br distances reported for bromine thioether CT adducts (2.3–2.4 Å).[10,11] The Ni–S1 bond lengths are also affected, on average these lengthen by 0.11 Å relative to **1**.

To our knowledge, no dibromine adduct of a nickel thiolate complex has been reported to date. However, a iodine adduct of a square-planar nickel thiolate complex $[NiL'\rightarrow I_2]$ (H_2L' = *N,N'*-bis(2-sulfonylmethylpropane)-1,5-diazacyclooctane) has been described by Darensbourg et al.[6] A dinuclear Mo_2S_2 complex in which each of the bridging sulfido ligands interacts with a I_2 molecule has also been reported.[12] It is interesting to note that in phosphorus chemistry (which displays many analogies with that of sulfur) there is only one example of a $R_3P\rightarrow Br_2$ adduct, and no $\{M(R_2P\rightarrow Br{-}Br)\}$ complex.

Complex **1** was treated with two equivalents of Br_2 in MeCN at 0 °C to access a bis(dibromine) adduct $[Ni_2L(OAc)\cdot(Br_2)_2][ClO_4]$ (**3**).[13] However, instead of **3** the dicationic sulfenyl bromide complex $[Ni_2L^{Br}(OAc)][Br_3]_2$ (**4**) was obtained as black crystals, albeit in low yield (< 30 %). Attempts to increase the yield of **4** by increasing the Br_2/**1** ratio did not really meet with success. Thus, performing the reaction with a Br_2/**1** ratio of 3:1 provided **4** in only marginally higher yield (45 % with respect to **1**), a fact attributable to the instability of the $[Ni_2L^{Br}(OAc)]^{2+}$ ion. At Br_2/**1** ratios larger than 3:1 the dark-brown color of the solution quickly fades and a yellow product of unknown composition precipitates. In solvents such as MeOH, EtOH or DMF, the formation of **4** was not observed.

Crystals of **4** are composed of $[Ni_2L^{Br}(OAc)]^{2+}$ ions (Figure 2a) and linear tribromide counterions with inequivalent bond lengths (Br–Br: 2.470(2), 2.623(2) and 2.493(2), 2.605(1) Å).[14] The S–Br distance of 2.268(2) Å is significantly shorter than in **2**, and approaches the 2.169(2)–2.255(5) Å range typical of covalent S–Br single bonds.[11,15] A Br1···Br2 distance of 3.129(1) Å is indicative of weak bonding interactions between the sulfenyl bromide complex and an adjacent Br_3^- ion (Figure 2b).

To our knowledge, this is the first structural report of a transition-metal complex of an arenesulfenyl bromide ligand.

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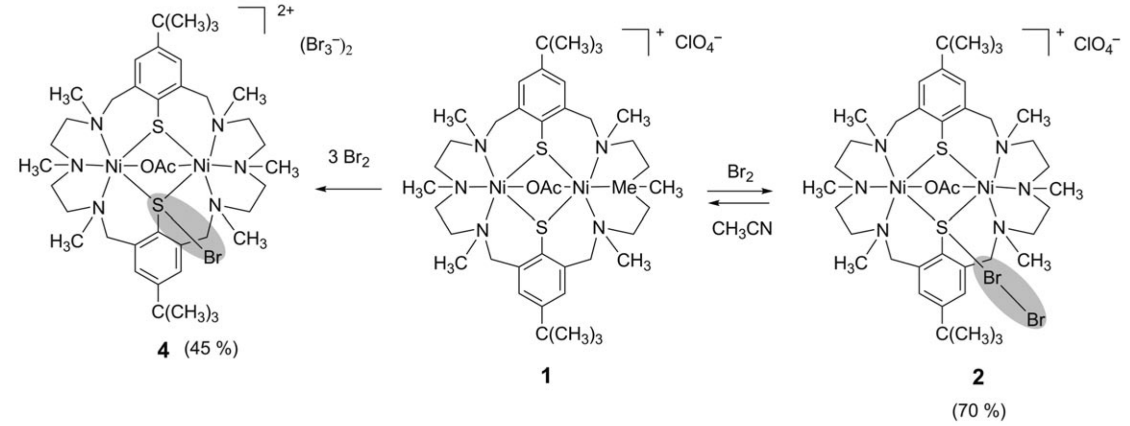

Scheme 1. Synthesis of the CT complex **2** and its conversion into the arenesulfenyl bromide complex **4**.

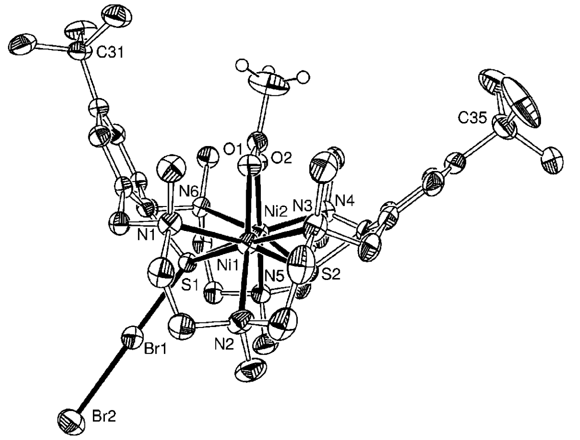

Figure 1. Side view of the molecular structure of complex **2** (thermal ellipsoids set at 50% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Br1-S1 2.401(1), Br1-Br2 2.6980(7), Ni1-O1 2.003(3), Ni1-N1 2.271(3), Ni1-N2 2.129(3), Ni1-N3 2.168(3), Ni1-S1 2.581(1), Ni1-S2 2.444(1), Ni2-O2 2.009(3), Ni2-N4 2.141(3), Ni2-N5 2.126(3), Ni2-N6 2.276(3), Ni2-S1 2.584(1), Ni2-S2 2.450(1), Ni···Ni 3.656(1); Ni1-S1-Ni2 90.12(3) Ni1-S2-Ni2 96.65(4), S1-Br1-Br2 178.51(3).

Only a dinuclear tungsten complex with a bridging bromosulfido ligand has been described.[16] The mean Ni–S^{Br} bond length (2.667(2) Å) is much longer than the Ni–S^{thiolate} bond length (2.439(2) Å) indicative of a greatly decreased electron-donating ability of the sulfenyl bromide.

A powdered sample of compound **2** does not lose Br$_2$ under vacuum (ca. 0.1 Torr, 60 °C, 6 h), but decomposes slowly over the course of several weeks forming a green-brown solid of unknown composition. Solid **4** remains stable for at least six months. Decomposition also occurs upon heating above 200 °C (**4**) or 280 °C (**2**) with no apparent evolution of dibromine (as determined by theromgravimetric analysis and differential scanning calorimetry). Both compounds are very unstable in solution and degrade within a few hours at ambient temperature to give colorless solutions.

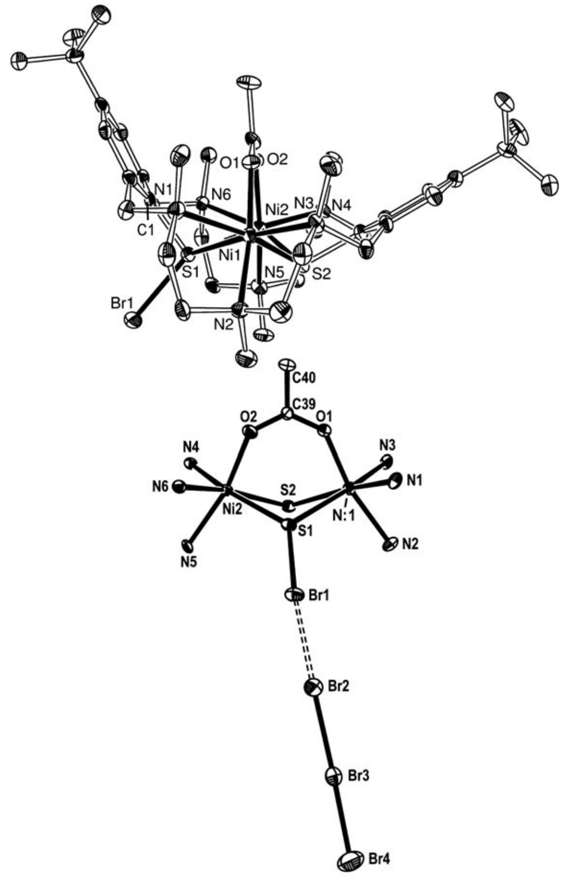

Figure 2. Top: Molecular structure of the [Ni$_2$L^{Br}(OAc)]$^{2+}$ ion in crystals of **4**. Right: Coordination polyhedra in **4** showing the secondary interaction between the sulfenylbromide and a neighboring Br$_3^-$ ion (dashed line). Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles Br1-S1 2.268(2), Br2-Br3 2.623(2), Br3-Br4 2.470(2), Br1···Br2 3.129(2), Ni1-O1 1.990(5), Ni1-N1 2.271(6), Ni1-N2 2.159(6), Ni1-N3 2.122(5), Ni1-S1 2.642(2), Ni1-S2 2.447(2), Ni2-O2 2.001(5), Ni2-N4 2.118(5), Ni2-N5 2.155(5), Ni2-N6 2.255(6), Ni2-S1 2.691(2), Ni2-S2 2.430(2), Ni1···Ni2 3.791(1); Ni1-S1-Ni2 90.64(5), Ni1-S2-Ni2 102.07(7), Br1-S1-Ni1 124.14(8), Br1-S1-C1 104.8(2), Br1-S1-Ni2 130.22(7), Br2-Br3-Br4 178.28(5), Br3-Br2···Br1 152.2(1).

Complexes **1**, **2**, and **4** have been investigated by FT-Raman spectroscopy; the spectra were very complex and are provided in the Supporting Information. The spectrum of **2** reveals two bands at 225 and 292 cm^{-1} which are not seen for **1** and presumably associated with the Br–Br (225 cm^{-1}) and S–Br (292 cm^{-1}) stretching vibrations, respectively. In the thioether–Br$_2$ CT adduct $(CH_3)_2SBr_2$ these modes occur at 211 and 289 cm^{-1}, respectively.[10] The large shift of the Br–Br stretching vibration away from that of the uncomplexed Br$_2$ molecule (301 cm^{-1})[17] is in agreement with a decrease of the Br–Br bond order and the CT nature of **2**. Complex **4** displays two Raman bands at 156 and 180 cm^{-1} attributable to the ν_s(BrBr) and ν_{as}(BrBr) stretching modes of the tribromide ions.[18] The band at 336 cm^{-1} is assumed to be the stretching vibration of the S–Br bond. This frequency is similar to those reported for $Me_2S{-}Br^+$ (346 cm^{-1})[10] and S_2Br_2 (357 cm^{-1}).[19] The shift of the S–Br stretch from 292 cm^{-1} in **2** to 336 cm^{-1} in **4** is in good agreement with the stronger (covalent) S–Br bonding interaction in **4**. We also note a red shift of the antisymmetric carboxylate stretching mode, ν_{as}(OAc), upon going from **1** (1588 cm^{-1}) to **2** (1582 cm^{-1}) and to **4** (1578 cm^{-1}). This red shift can be traced back to the charge transfer from the thiolate into the antibonding Br$_2$ σ^* orbital or the formation of an S–Br single bond, respectively. The decrease of the charge on the S atom increases the effective charge on the two Ni^{II} ions. This in turn strengthens the Coulomb interactions between the acetate and the nickel ions in **2** and results in the observed frequency shifts. A similar effect has been observed for a series of carboxylato-bridged Co$^{II}_2$ and Co$^{III}_2$ complexes of L^{2-}.[20]

The UV/Vis and ESI mass spectrometric studies (see Supporting Information) are indicative of relatively weak S→Br$_2$ and S–Br bonds thus rendering solution techniques (UV/Vis, MS) for characterization of **2** and **4** inappropriate. Similar observations have been made for other halogen–sulfur CT adducts.[2]

Temperature-dependent magnetic susceptibility measurements for **2** and **4** were carried out to examine their electronic structures. Figure 3 shows the results in the form of μ_{eff} versus T plots. Data for $[LNi_2(OAc)][BPh_4]$ are included for comparison.[21] For **2**, the effective magnetic moment (per dinuclear complex) increases from 4.68 μ_B at 295 K to a maximum value of 4.97 μ_B at 18 K and then decreases to 4.31 μ_B at 2.0 K. This behavior indicates an intramolecular ferromagnetic exchange interaction between the two divalent Ni^{II} ions in **2**.[22] The steady decrease for **4** on the other hand indicates an intramolecular antiferromagnetic exchange interaction. Least-squares fits of the magnetic susceptibility data by full-matrix diagonalization of the appropriate spin Hamiltonian gave $J = 5.2$ cm^{-1}, $D = -27.7$ cm^{-1}, and $g = 2.09$ (for **2**) and $J = -0.3$ cm^{-1}, $D = -59.0$ cm^{-1}, and $g = 2.17$ (for **4**). Thus the conversion of **2** into **4** is accompanied by a change of the spin ground state from $S = 2$ to $S = 0$.

In summary, the first examples for nickel thiolate Br$_2$ charge transfer complexes and their corresponding sulfenylbromide derivatives have been isolated and structurally characterized. This study is of relevance for the activation and transformation of small molecules by dinuclear transition-metal thiolate complexes, and is an important addition to the chemistry of sulfenyl halides.

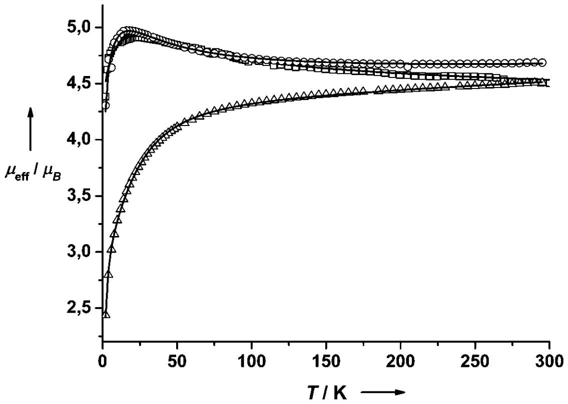

Figure 3. Temperature dependence of μ_{eff} for **1** with BPh$_4^-$ instead of ClO$_4^-$ as counterion (□), **2** (○), and **4** (△). The solid line represents the best theoretical fit of the magnetic susceptibility data by full-matrix diagonalization of the appropriate spin Hamiltonian $H = -2J S_1 S_2 + D(S_{z1}^2 + S_{z2}^2 - 4/3) + g\beta(S_1 + S_2)B$.

Experimental Section

For experimental details, see the Supporting Information.

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[1] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**, p. 552.

[2] a) A. J. Blake, R. O. Gould, C. Radek, M. Schröder, *J. Chem. Soc. Chem. Commun.* **1993**, 1191–1193; b) A. J. Blake, F. A. Devillanova, A. Garau, L. M. Gilby, R. O. Gould, F. Isaia, V. Lippolis, S. Parsons, C. Radek, M. Schröder, *J. Chem. Soc. Dalton Trans.* **1998**, 2037–2046.

[3] H. Bock, Z. Havlas, A. Rauschenbach, C. Näther, M. Kleine, *Chem. Commun.* **1996**, 1529–1531.

[4] M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, F. Isaia, F. Lelj, V. Lippolis, G. Verani, *Chem. Eur. J.* **2001**, *7*, 3122–3133.

[5] E. Kühle, *Synthesis* **1971**, 617–638.

[6] E. J. Lyon, G. Musie, J. H. Reibenspies, M. Y. Darensbourg, *Inorg. Chem.* **1998**, *37*, 6942–6949.

[7] B. Kersting, *Angew. Chem.* **2001**, *113*, 4109–4112; *Angew. Chem. Int. Ed.* **2001**, *40*, 3987–3990.

[8] Crystal data for $\mathbf{2}\cdot CH_3CH_2CN$: $C_{43}H_{72}Br_2ClN_7Ni_2O_6S_2$, $M_r = 1159.89$, monoclinic, space group $P2_1/c$, $a = 15.116(2)$, $b = 23.395(4)$, $c = 16.229(2)$ Å, $\beta = 114.25(3)°$, $V = 5233(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.472$ g cm^{-3}; $T = -60$ °C, $\mu(Mo_{K\alpha}) = 2.427$ mm^{-1} ($\lambda = 0.71073$ Å); 32246 reflections measured, 12470 unique, 7318 with $I > 2\sigma(I)$, refinement converged to $R = 0.0432$, $wR = 0.1061$ ($I > 2\sigma(I)$), 633 parameters and 144 restraints, ClO$_4^-$ and a *t*Bu group are disordered over two sites, min./max. residual electron density = +1.869/–0.993 e Å^3. The one large residual peak (1.87 e$^-$ Å^3) in the final Fourier map is located in the vicinity

of the Br(2) atom (d(Br2···Q1) = 1.19 Å). The electron density map is otherwise featureless. CCDC-694585 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[9] a) R. Minkwitz, U. Nass, H. Preut, *Z. Anorg. Allg. Chem.* **1986**, *538*, 143–150; b) R. Minkwitz, R. Lekies, A. Radünz, H. Oberhammer, *Z. Anorg. Allg. Chem.* **1985**, *531*, 31–40.

[10] a) B. Regelmann, K. W. Klinkhammer, A. Schmidt, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1633–1638; b) G. B. M. Vaughan, A. J. Mora, A. N. Fitch, P. N. Gates, A. S. Muir, *J. Chem. Soc. Dalton Trans.* **1999**, 79–84.

[11] M. Gonsior, I. Krossing, *Chem. Eur. J.* **2004**, *10*, 5730–5736.

[12] J. Allshouse, R. C. Haltiwanger, V. Allured, M. R. DuBois, *Inorg. Chem.* **1994**, *33*, 2505–2506.

[13] A bis(diiodine)adduct of **1**, that is, ([$Ni_2L(OAc)\cdot(I_2)_2$][ClO_4]), has been prepared and structurally characterized. Each thiolate residue interacts with one diiodine, the S-I and I-I distances being 2.805 Å (S1–I1), 2.939 Å (S2–I3), 2.818 Å (I1–I2), and 2.770 Å (I3–I4), respectively. These results will be reported elsewhere.

[14] Crystal data for **4**: $C_{40}H_{67}Br_7N_6Ni_2O_2S_2$, $M_r = 1404.91$, triclinic, space group $P\bar{1}$, $a = 13.725(3)$, $b = 14.032(3)$, $c = 14.198(3)$ Å, $\alpha = 75.25(3)°$, $\beta = 78.62(3)°$, $\gamma = 85.74(3)°$, $V = 2591.5(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.800$ g cm^{-3}; $T = -160$ °C, $\mu(Mo_{K\alpha}) = 6.243$ mm^{-1} ($\lambda = 0.71073$ Å); 24705 reflections measured, 12891 unique, 8390 with $I > 2\sigma(I)$, refinement converged to $R = 0.0679$, $wR = 0.1296$ ($I > 2\sigma(I)$), 532 parameters and 0 restraints, min./max. residual electron density = +2.027/−1.139 e Å^3. The three large residual peaks (2.03–1.44 e Å^3) in the final Fourier map of **4** are located in the vicinity of a Br_3^- ion (Q1–Q3; d(Br···Q) < 1.5 Å). The electron density map is otherwise featureless. CCDC 694586 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] a) E. Hirota, *Bull. Chem. Soc. Jpn.* **1958**, *31*, 130–138; b) C. O. Della Vedova, H.-G. Mack, *Inorg. Chem.* **1993**, *32*, 948–950; c) J. Passmore, G. W. Sutherland, T. K. Whidden, P. S. White, C.-M. Wong, *Can. J. Chem.* **1985**, *63*, 1209–1214; d) T. Klapötke, J. Passmore, *Acc. Chem. Res.* **1989**, *22*, 234–240.

[16] J. Q. Lee, M. L. Sampson, J. F. Richardson, M. E. Noble, *Inorg. Chem.* **1995**, *34*, 5055–5064.

[17] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsfrequenzen I, Hauptgruppenelemente*, Georg Thieme, Stuttgart, **1991**.

[18] G. R. Burns, R. M. Renner, *Spectrochim. Acta Part A* **1991**, *47*, 991–999.

[19] C. A. Frenzel, K. E. Blick, *J. Chem. Phys.* **1971**, *55*, 2715–2719.

[20] B. Kersting, G. Steinfeld, *Inorg. Chem.* **2002**, *41*, 1140–1151.

[21] Y. Journaux, T. Glaser, G. Steinfeld, V. Lozan, B. Kersting, *Dalton Trans.* **2006**, 1738–1748.

[22] In the solid state the dinuclear nickel complexes are well-separated from each other by the ClO_4^- ions. The abrupt decrease in μ_{eff} below 18 K is therefore most likely due to zero-field splitting of Ni^{II} and not to intermolecular exchange interactions.