temperature in the range of -50 to $-70\,^{\circ}C$ and treated with pure O_2 to yield a deep red solution. Within 5–10 min a precipitation of a deep red microcrystalline substance **2** (0.12 g; 19%) occurred. An alternative method for crystallizing **2** was to add 30% H_2O_2 (0.26 mL) to a solution of **1** (160 mg, 2.23 mmol) in CH_3OH (25 mL) at $-80\,^{\circ}C$. C, H, N, Cu analyses (%; $C_{34}H_{57}N_2O_4Cu$): calcd (found): C 65.72 (65.45), H 9.25 (9.23), N 4.51 (4.52), Cu 10.23 (10.20); UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$L\,mol^{-1}\,cm^{-1}$]) = 391 (2.1×10^3), 423 (1.8×10^3), 524 (2.1×10^3), 649 (1.6×10^3); ^1H NMR (CD_2Cl_2, 400 MHz): $\delta = 0.99$ (t, 9H), 1.18 (s, 18H), 1.29 (s, 18H), 1.80 (br. s, 2H), 2.50 (dt, 6H), 7.20 (s, 2H), 7.33 (s, 2H).

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[6] Kitajima et al. have reported the structure of the mononuclear, diamagnetic superoxocopper(II) complex $[Cu^{II}(O_2^{\cdot-})(HB(3\text{-}t\text{Bu-}5\text{-}i\text{Pr-pyrazole})_3)]$ with a coordinated $O_2^{\cdot-}$ ligand in "side-on" mode ($\tilde{\nu}(^{16}O_2)$ 1111 cm^{-1} and $\tilde{\nu}(^{18}O_2)$ 1062 cm^{-1}): K. Fujisawa, M. Tanaka, Y. Moro-oka, N. Kitajima, *J. Am. Chem. Soc.* **1994**, *116*, 12079. We consider **2** to contain an "end-on" coordinated $O_2^{\cdot-}$, which is evident from the isotope labeling of **2** with $^{16}O-^{18}O$. A broad asymmetric band for $\tilde{\nu}(Cu\text{-}^{16}O\text{-}^{18}O)$ at 939 cm^{-1} (due to superposition of two bands at 942 and 932 cm^{-1} for the isotopomers $Cu^{16}O\text{-}^{18}O$ and $Cu\text{-}^{18}O\text{-}^{16}O$, respectively, is observed. a) A. Nakamura, Y. Tatsuno, M. Yamamoto, S. Otsuka, *J. Am. Chem. Soc.* **1971**, *93*, 6052; b) J. E. Pate, R. W. Cruse, K. D. Karlin, E. I. Solomon, *J. Am. Chem. Soc.* **1987**, *109*, 2624. The single structurally characterized hydroperoxocopper(II) complex $[Cu^{II}(bppa)(OOH)]^+$ (bppa = bis(6-pivalamide-2-pyridylmethyl)(2-pyridylmethyl)amine) exhibits a $\tilde{\nu}(^{16}O_2)$ stretch at 856 cm^{-1} ($\tilde{\nu}(^{18}O_2) = 810$ cm^{-1}): A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, M. Masuda, M. Mukai, T. Kitagawa, H. Einaga, *Angew. Chem.* **1998**, *110*, 874; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 798.

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[8] X-ray analysis reveals an asymmetric electron density distribution in the $Cu(L^2)$ moiety of **1**. The C–N bond lengths are different owing to a substantial portion of double-bond character in N(1)–C(15) (1.358(2) Å). This description is additionally supported by the EPR spectra of the isostructural Zn^{II} complex, $[Zn(L^2)(NEt_3)]$, in which there is significantly different spin density at the two *para* carbon atoms with respect to the imino nitrogens. P. Chaudhuri, M. Hess, K. Hildenbrand, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* submitted.

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[10] The temperature-dependent magnetic moments for **1** were fitted without problem to the theoretical curve based on the exchange Hamiltonian $\boldsymbol{H} = -2J\mathbf{S}_{Cu}\mathbf{S}_{Lig.}$ ($S_{Cu} = S_{Lig} = ½$) for evaluating the exchange coupling constant $J = -137$ cm^{-1}: In an idealized C_{2v} symmetry a substantial portion of the antibonding effect of the original e_g orbitals is removed to the metal–ligand bond, together with a mixing of metal x and z components in the orbitals of the molecule. Thus the unpaired electron of Cu in **1** residing in a $2a_1$ orbital can overlap with the half-occupied π orbital of the radical ligand resulting in antiferromagnetic coupling. T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley-Interscience, New York, **1985**. Compound **2** is diamagnetic ($S = 0$) in the temperature range 2–300 K.

[11] Kinetic experiments were performed at $20\,^{\circ}C$ in an open vessel with stirring under air. Formation of aldehydes (GC/^1H NMR) and H_2O_2 (spectrophotometry)[1] was monitored (initial-rate method) as a function of time: $[CuCl] = [\{H_4(L^3)\}(CF_3CO_2)] = 7.5\times10^{-4}-7.5\times10^{-3}$ M; [alcohol] = 0.025–1.25 M; $[NEt_3] = 2.0\times10^{-3}$ M = constant.

Synthesis, Structure, and Redox Properties of $[\{(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)\}_2Mo(CO)_2]$, a Novel Metalladithiolene Cluster**

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Dithiolato complexes of late transition metals exhibit interesting physical and chemical properties such as reversible redox activity, deep colors,[1] and various substitution and addition reactions due to the quasiaromaticity and electronic unsaturation of the metalladithiolene ring.[2] However, no reports on metal–metal bond formation by metalladithiolene complexes are available to our knowledge. Here we report the first formation of a cluster from a cobalt dithiolene complex, namely, $[CoCp(S_2C_6H_4)]$ (**1**, $Cp = \eta^5\text{-}C_5H_5$), by reaction with $[Mo(CO)_3(py)_3]$ and BF_3 to give $[\{CpCo(S_2C_6H_4)\}_2Mo(CO)_2]$ (**2**), which has an almost linear Co-Mo-Co arrangement and four μ-S bridges. It can be regarded as two cobaltadithiolene rings bridged by a molybdenum dicarbonyl moiety. The redox

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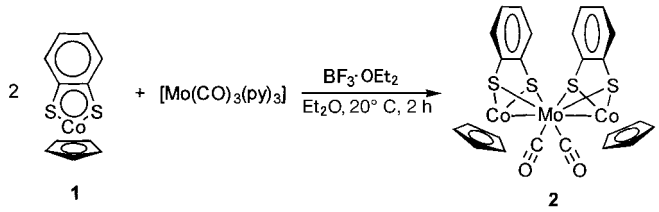
properties of **2** could indicate how the Co–Co electronic interaction is transmitted by the Mo atom, since cobaltadithiolene undergoes a reversible one-electron reduction.[3]

The mixed-metal cluster **2** was obtained by reaction of two equivalents of **1** with one equivalent of $[Mo(CO)_3(py)_3]$ in the presence of more than three equivalents of BF_3 in diethyl ether at room temperature (Scheme 1). The combination of



Scheme 1. Synthesis of **2**.

$[Mo(CO)_3(py)_3]$ and BF_3 is an effective way of generating a reactive $[Mo(CO)_3]$ moiety that can bind to arenes.[4] However, we could not detect any products in which the benzene ring ligates to Mo, even at different **1**/$[Mo(CO)_3(py)_3]$ molar ratios. This is presumably due to the higher reactivity of the electronically unsaturated cobaltadithiolene ring for addition reactions compared to the benzene ring. We assume that $[Mo(CO)_3]$ adds to **1** to give a 1:1 complex with a Co–Mo and two Co-S-Mo bonds, but because this complex has an odd number of electrons at Mo, it reacts with a further molecule of **1** with loss of CO to give the 2:1 complex **2**.

The crystal structure of **2** is displayed in Figure 1.[5] The Mo center is eight-coordinate with a square-antiprismatic (or dodecahedral) geometry, and the two S-Mo-S planes are twisted by 28.17° with resect to one another. The coordination

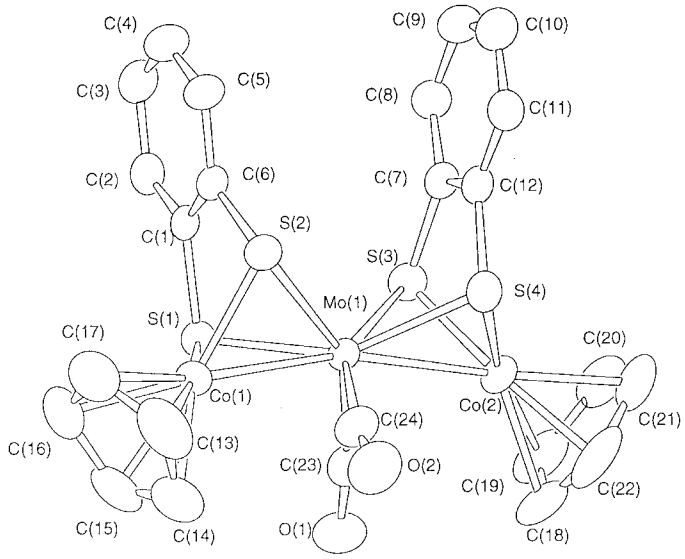


Figure 1. ORTEP plot of **2** with 50% probability ellipsoids. Selected bond lengths [Å] and angles [°]: Mo1–Co1 2.6182(8), Mo1–Co2 2.6327(9), Mo1–S1 2.478(1), Mo1–S2 2.520(1), Mo1–S3 2.514(1), Mo1–S4 2.477(1), Co1–S1 2.199(2), Co1–S2 2.237(2), Co2–S3 2.227(2), Co2–S4 2.191(2); Co1-Mo1-Co2 165.03(3), Co1-Mo1-S1 51.04(4), Co1-Mo1-S2 51.58(4), Mo1-C23-O1 171.8(5).

environment of the Mo center with respect to the nonmetallic ligands (S and CO) is distorted trigonal-prismatic. Hence, the molecule belongs to the point group C_2. The cobaltadithiolene rings are nonplanar owing to the coordination of the S atoms to Mo. The Co–S bond length of 2.218 Å is 0.107 Å longer than that of a free cobaltadithiolene ring.[6] The Co–Mo bond length is 2.625 Å, which lies in the usual range for Co–Mo single bonds.[7] The number of total valence electrons around the Co_2Mo core is 50; the four S atoms each contribute three electrons.

In the IR spectrum of **2**, two ν(CO) bands are observed, and this is consistent with the C_2 symmetry at the Mo center. In the electronic spectrum of **2**, a strong absorption band is observed at $\lambda_{max} = 476$ nm ($\varepsilon = 9800\ mol^{-1}\,dm^3\,cm^{-1}$). A preliminary molecular orbital calculation for **2** by the DV-Xα method indicates that this band is characteristic of metal-to-metal charge transfer (MMCT) from Mo to Co rather than ligand-to-metal charge transfer (LMCT),[8] because the energy levels of the d orbitals of Mo are close to those of Co. The ^{1}H NMR signals of the benzene rings of **2** appear at $\delta = 6.34$ and 6.79 and are shifted upfield by 0.79 and 1.30 ppm, respectively, relative to those of **1**. This effect can be attributed to the ring currents of the benzene rings.

A cyclic voltammogram of **2** in $[Bu_4N][ClO_4]$/MeCN is shown in Figure 2. The first cyclic scan between -0.4 and -1.8 V versus Ag/Ag^+ shows two couples of reduction and

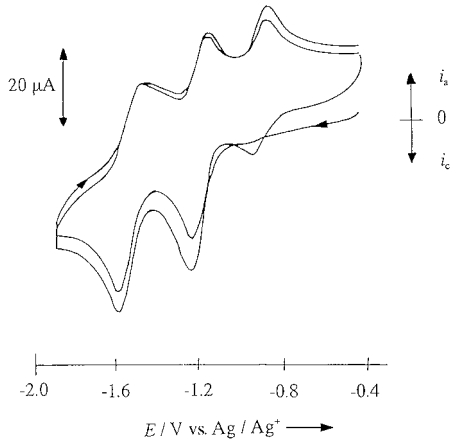


Figure 2. Cyclic voltammogram of **2** at a glassy carbon electrode in 0.1 mol dm^{-3} $[Bu_4N][ClO_4]$/MeCN at a scan rate of 0.1 V s^{-1}.

reoxidation waves at $E^{0\prime} = -1.20$ and -1.53 V and an oxidation wave at $E_{p,a} = -0.90$ V. A reduction wave corresponding to this oxidation wave is observed at $E_{p,c} = -0.96$ V in the second cyclic scan. This additional redox couple was assigned to **1**/**1**$^-$ by comparison of the $E^{0\prime}$ values and UV/Vis absorption spectra of **1** and the electrolysis product of **2**. The redox wave due to **1**/**1**$^-$ does not appear when the negative limit of the potential scan is -1.4 V, which causes only the first reduction step of **2**. These results indicate that reduction of **2** gives successively the monoanion and dianion, after which the dianion decomposes to two monanions of **1** and a $[Mo(CO)_2]$ fragment, the fate of which has not been determined. Thus, the redox process of **2** can be expressed as the EEC mechanism given in Equations (1) – (3).

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$$\mathbf{2} + e^- \overset{E_1^{0'}}{\rightleftharpoons} \mathbf{2}^- \quad (1)$$

$$\mathbf{2}^- + e^- \overset{E_2^{0'}}{\rightleftharpoons} \mathbf{2}^{2-} \quad (2)$$

$$\mathbf{2}^{2-} \overset{k}{\rightarrow} 2\,\mathbf{1}^- + \text{'[Mo(CO)}_2\text{]'} \quad (3)$$

The two redox potentials and the rate constant of the decomposition reaction of $\mathbf{2}^{2-}$ were estimated by computer simulation to be $E_1^{0'} = -1.20$ V, $E_2^{0'} = -1.53$ V, and $k = 0.19\ s^{-1}$. On the basis of these redox potentials, it is reasonable to assume that not the Mo atom but the two Co centers undergo reduction. Hence, the valence balance of $\mathbf{2}^-$ can be roughly expressed as $Co^{III}Mo^0Co^{II}$, which suggests that the Mo bridge assists electronic interaction between the Co sites to form a thermodynamically favorable mixed-valence state. This is supported by the electronic spectrum of $\mathbf{2}^-$, generated by the reduction of **2** with Na in THF, in which a broad band at 1160 nm ($\varepsilon = 60\ mol^{-1}\,dm^3\,cm^{-1}$) is attributed to intervalence transfer.[9] Detailed studies on the optical and magnetic properties of the reduced forms of **2** are in progress

Experimental Section

2: All manipulations were carried out under nitrogen or argon. $BF_3 \cdot OEt_2$ (0.134 mL, 95.0 %, 1.0 mmol) was added dropwise to a stirred solution of **1**[10] (0.106 g, 0.40 mmol) and $[Mo(CO)_3(py)_3]$[11] (0.084 g, 0.20 mmol) in diethyl ether (30 mL) at room temperature, and the mixture was stirred for 2 h. The solvent was evaporated under vacuum, and the components of the residue were separated by thin-layer chromatography on silica gel with toluene/hexane (2/1) as eluent. The component in the first band was eluted with toluene and recrystallized from hexane to give 50 mg (0.074 mmol, 37 %) of fine brown crystals of **2**. Elemental analysis calcd for $C_{24}H_{18}Co_2MoO_2S_4$ (%): C 42.39, H 2.99, S 18.85; found: C 42.18, H 2.82, S 18.59; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): $\delta = 5.15$ (s, 10H, Cp), 6.34 (dd, J(H,H) = 5.5, 3.3 Hz, 4H, Ph), 6.79 (dd, 4H, Ph); IR (KBr disk): $\tilde{\nu} = 1860$, 1923 cm^{-1} (CO).

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[5] X-ray strucure analysis of **2**: A crystal ($0.20 \times 0.20 \times 0.60$ mm) was mounted in a glass capillary, and data were collected at 296 K on a Rigaku AfC7R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å) and rotating-anode generator. Crystal data: $C_{24}H_{18}O_2MoCoS_4$, $M_r = 680.45$, triclinic, space group $P\bar{1}$, $a = 12.040(3)$, $b = 15.858(4)$, $c = 6.587(2)$ Å, $\alpha = 101.89(2)$, $\beta = 98.86(2)$, $\gamma = 92.78(2)^\circ$, $V = 1211.8(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.865\ g\,cm^{-3}$; of 7381 reflections ($6 < 2\theta < 60^\circ$), 7068 were unique. The linear absorption coefficient μ for $Mo_{K\alpha}$ radiation is 22.3 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied and resulted in transmission factors ranging from 0.88 to 1.00. The data were corrected for Lorentzian and polarization effects. The structure was solved by direct methods and expanded by Fourier techniques. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4707 observed reflections ($I > 3\sigma(I)$) with unweighted and weighted agreement factors of $R = 0.041$ and $R_w = 0.040$. All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-108002. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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The Synthesis and Molecular Structure of the First Two-Coordinate, Dinuclear σ-Bonded Mercury(I) RHgHgR Compound**

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In memory of Nicolai S. Vyazankin

Most of the known mercury compounds have a formal +2 oxidation state.[1–5] σ-Bonded organomercury(I) compounds with a +1 oxidation state for example RHgHgR, R = organic substituent, have been frequently cited in the literature as

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