A New Synthetic Strategy for Magnetic Metal Bis(dithiolene) Based Conductors

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The combination of the $[Co^{III}(Cl_2\text{-bpy})_3]^{3+}$ complex with the $[Ni(dmit)_2]^-$ anion is a one-step reaction, which results in the partially oxidised $Ni(dmit)_2$-based material $[Co^{II}(Cl_2\text{-bpy})_3][Ni(dmit)_2]_5$ with a paramagnetic Co^{II} cation, as proven by Raman, EPR and XAS, exemplifying a, for $M(dithiolene)_2$ compounds new, synthetic strategy that may give access to a large variety of new $[Co^{II}(N,N\text{-imine})_3][M(dithiolene)_2]_n$ ($n > 2$, M = Ni, Pd) type magnetic conductors.

Introduction

One of the important relatively recent challenges in the design of molecular conductors is the combination of magnetic and conducting properties.[1] In the area of $M(dmit)_2$-based (M = Ni, Pd; dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) compounds, attempts to obtain these multiple-property materials have been made by combination of the $M(dmit)_2$ anion with either an organic radical cation[2−4] or with a paramagnetic transition-metal cation. Apart from $Cu_{0.39}[Ni(dmit)_2]$ reported by Sakai et al.,[5] no previously published $M(dmit)_2$-based material contains both (1) a paramagnetic transition-metal cation and (2) an $[M(dmit)_2]^{x-}$ anion with a non-integer formal charge ($0 < x < 1$), which is the best electronic situation for optimal conductivity.[6] Most reported $M(dmit)_2$-based materials containing a transition-metal cation are $[M'(Cp^*)_2][M(dmit)_2]$ (M′ = Fe, Mn, Ni) type compounds[7−10] with monovalent anions. These compounds exhibit various magnetic properties. Nevertheless, they can be considered precursors that need further oxidation, required to obtain a species with a non-integer formal charge. However, the major problem of these precursor materials is their poor solubility in most organic solvents, making subsequent chemical or electrolytic oxidation of the anion, virtually impossible.

Here we present an elegant and powerful solution to this problem: combination of the $[M(dmit)_2]^{1-}$ anion with an oxidant that becomes a paramagnet upon its reduction and that subsequently precipitates together with the oxidised $[M(dmit)_2]^{x-}$ ($0 < x < 1$) anion, resulting in a fractionally oxidised, $M(dmit)_2$-based material containing a paramagnetic cation.

There are only a few examples in the literature where this concept of using a counter ion as an oxidant for the potentially conducting species has been exploited. $[BEDT\text{-}TTF]_{3.6}[MnCl_4]$ is an insulating compound. Replacement of some $[Mn^{II}Cl_4]^{2-}$ anions ($S = 5/2$) by $[Fe^{III}Cl_4]^-$ anions ($S = 5/2$) results in the Fe-doped salt $[BEDT\text{-}TTF]_{3.6}[(MnCl_4)_{1-x}(FeCl_4)_x]$ ($x = 0.05$) with strongly reduced resistivity and a magnetic behaviour composed of the Curie−Weiss contribution of the anions and Pauli contribution of mobile electrons in the donor lattice.[11] The semiconducting ($\sigma_{rt} = 0.025\ S\,cm^{-1}$) antiferromagnet $TMTSF(FeCl_4)$ is the product of the oxidation of the neutral TMTSF molecule to the $TMTSF^{\cdot+}$ radical cation by two $Fe^{III}Cl_3$ units that are converted into the paramagnetic counteranion $[Fe^{III}Cl_4]^-$ and "waste product" $Fe^{II}Cl_2$.[12] The compounds $(TTF)_6(Et_4N)(HPMo_{12}O_{40})$ and $(TTF)_6(Et_4N)(HPW_{12}O_{40})$ ($\sigma_{rt} = 10^{-3}{-}10^{-4}\ S\,cm^{-1}$) also are the result of a redox reaction between the $[PM_{12}O_{40}]^{3-}$ (M = W, Mo) anions that act as oxidants for the neutral TTF donor.[13] The redox reaction generates a paramagnetic $[PM_{12}O_{40}]^{4-}$ anion and a radical cation $TTF^{\cdot+}$. Already in 1980 some semiconducting $[CuL](TCNQ)_2$ and $[CuL_2](TCNQ)_2$ compounds ($\sigma_{rt} = 10^{-7}{-}1.9\ S\,cm^{-1}$) have been reported with L = en, bpy, phen. Some of these $Cu^{II}L$ and $Cu^{II}L_2$ complexes act as oxidants for the TCNQ anions, resulting in compounds with a charge distribution be-

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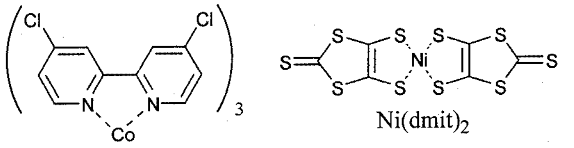
tween $Cu^{II}Ln(TCNQ^{-})_2$ and $Cu^{I}Ln(TCNQ^{-})(TCNQ^{0})$, which eliminates the paramagnetism of some of the Cu^{II} species, since the Cu^{I} d^{10} species are diamagnetic. However, these compounds do display coexistence of magnetic and conducting properties.[14–17] In the case of the $[Cu^{I}\{bis(2\text{-}pyridyl)amine\}_2][TCNQ]_2$ this redox reaction is total, resulting in fractionally oxidized anions and a diamagnetic cation.[18,19]

In this communication we present, for the first time with the $[Ni(dmit)_2]^{-}$ anion, such a redox reaction, where the oxidant, a cobalt(III) cation, becomes the paramagnetic species and the $[Ni(dmit)_2]^{-}$ complex anion, the fractionally oxidised, potentially conducting species. Octahedral cobalt(III) complexes with 6 nitrogen donor atoms are d^6 systems with in general a low-spin $t_{2g}{}^6e_g{}^0$ ($S = 0$) ground state. The Co^{II} equivalent, however, is a d^7 system with a high-spin $t_{2g}{}^5e_g{}^2$ ($S = 1.5$) ground state.[20] Therefore, reduction of the Co^{III} starting compound is absolutely indispensable in order to obtain a paramagnetic cation. The electron for this reduction can be provided by the $[Ni(dmit)_2]^{-}$ anion, which then can be oxidised to its neutral form. This species then can recombine with other anions[21] to form an array of $Ni(dmit)_2$ units with formal fractional charge $x-$ ($0 < x < 1$), an optimal situation for conductivity. The desired redox reactions are described in Scheme 1.



$$[Co(III)(Cl_2\text{-}bpy)_3]^{3+} + e^{-} \text{--->} [Co(II)(Cl_2\text{-}bpy)_3]^{2+} \quad E_{1/2} = 0.60\ V$$

$$1/(1\text{-}x)\ [Ni(dmit)_2]^{1-} \text{--->} 1/(1\text{-}x)\ [Ni(dmit)_2]^{x-} + e^{-} \quad E_{ox} = 0.24\ V$$

Scheme 1. Structure and redox reactions of $[Co^{III}(Cl_2\text{-}bpy)_3]^{3+}$ ($E_{1/2}$ determined here) and $[Ni(dmit)_2]^{-}$ (E_{ox} redetermined here; see also ref.[22])

Below are the results of the combination of the $[Ni(dmit)_2]^{-}$ with a cationic complex that possesses these extraordinary capabilities: the $[Co^{III}(Cl_2\text{-}bpy)_3]^{3+}$ complex (Cl_2-bpy = 4,4′-dichloro-2,2′-bipyridine). The $[Co^{III}(bpy)_3]^{3+}$ also has been used for comparison.

Results and Discussion

The electrochemical potentials of the starting compounds $[Co^{III}(Cl_2\text{-}bpy)_3](PF_6)_3(H_2O)$, $[Co^{III}(bpy)_3](PF_6)_3(H_2O)$ and $[Bu_4N][Ni(dmit)_2]$ have been (re)determined[22,23] with cyclic voltammetry (WE, CE: Pt; RE: Ag/AgCl; CH_3CN/Bu_4NPF_6). Figure 1 shows their cyclic voltammograms. The half-wave potentials $E_{1/2,Co(III/II)}$ of $[Co(bpy)_3]^{3+}$, $E_{1/2}$ = 0.33 V vs. Ag/AgCl, and $[Co(Cl_2\text{-}bpy)_3]^{3+}$, $E_{1/2}$ = 0.60 V vs. Ag/AgCl, are both higher than the oxidation-wave potential E_{ox} of the $[Ni(dmit)_2]^{1-/x-}$ oxidation, E_{ox} = 0.24 V vs. Ag/AgCl. The difference between the half-wave potential of the oxidant and the reductant, $\Delta E = E_{1/2}([Co(L)_3]^{3+/2+}) - E_{ox}([Ni(dmit)_2]^{x-/1-})$ should be at least $\Delta E > 0.1$ V,[24] in order to have a charge transfer from anion to cation. The potential differences for $[Co(bpy)_3]^{3+}$ are $\Delta E = 0.09$, too small for this complex to be an oxidant for the $[Ni(dmit)_2]^{1-}$ anion, and for $[Co(Cl_2\text{-}bpy)_3]^{3+}$ $\Delta E = 0.36$ V. Therefore, the redox reactions shown in Scheme 1 were expected to occur only for the latter cation complex. The electron-withdrawing effect of the chlorine substituents on the bpy ligand in $[Co^{III}(Cl_2\text{-}bpy)_3]^{3+}$ apparently makes the difference between a normal counter cation and an effective oxidant for the $Ni(dmit)_2$ species.

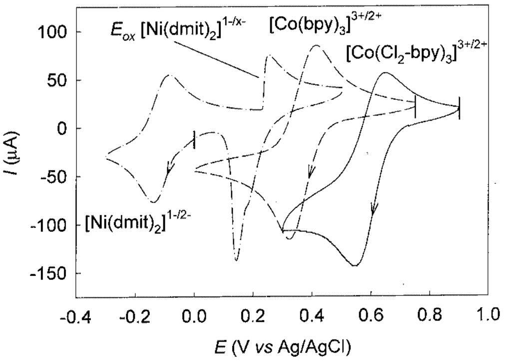


Figure 1. Cyclic voltammograms (WE, CE: Pt; RE: Ag/AgCl; CH_3CN/Bu_4NPF_6) of $[Bu_4N][Ni(dmit)_2]$ (−·), $[Co^{III}(bpy)_3](PF_6)_3{\cdot}H_2O$ (− −) and $[Co^{III}(Cl_2\text{-}bpy)_3](PF_6)_3{\cdot}H_2O$ (−)

Solutions of $[Co^{III}(Cl_2\text{-}bpy)_3](PF_6)_3(H_2O)$ or $[Co^{III}(bpy)_3](PF_6)_3(H_2O)$ and $[Bu_4N][Ni(dmit)_2]$ in acetone have been mixed and the resulting black precipitates (product A or B, respectively) have been filtered off and washed with acetone.

In order to determine whether $[Ni(dmit)_2]^{-}$ is oxidised in the products A and B, Raman spectroscopy has been performed. Raman is a useful tool to determine the effective charge on an $Ni(dmit)_2$ anion, because of the almost linear correlation between the frequency of the ν(C=C) vibration of the dmit ligand and the charge on the anion complex.[25] The cobalt oxidation state was determined using EPR and X-ray absorption spectroscopy (XAS) at the Co $L_{2,3}$ edges. XAS is a spectroscopic technique that is very sensitive to differences in charge and spin state of a metal cation.[26]

The Raman spectra of A, [$\tilde{\nu}$(C=C) = 1331 cm^{-1}], B [$\tilde{\nu}$(C=C) = 1391 cm^{-1}] and reference $[Bu_4N][Ni(dmit)_2]$ [$\tilde{\nu}$(C=C) = 1394 cm^{-1}] (Figure 2) indicate the presence of an oxidised $Ni(dmit)_2$ species in A and a normal monovalent anion in B. This suggests that oxidation of the anion occurred only during the formation of A. The effective charge on the oxidised species in A should be 0.03− based on the previously reported correlation.[25] The asymmetry of the 1331 cm^{-1} band may indicate some variation in charge on the oxidised $Ni(dmit)_2$ species. Also some signals with low intensity are present around 1390 cm^{-1} and higher, indicating an inhomogeneous charge distribution over the $Ni(dmit)_2$ complexes in product A.

Since the Co^{III} starting compounds are diamagnetic, the equivalent Co^{II} complexes have been used as references for the EPR spectra of A and B (X-band, dpph as a standard, T = 77 K), that are shown together with the spectrum of

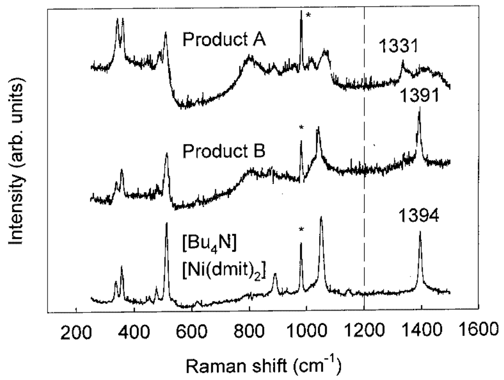


Figure 2. Raman spectra of powdered samples in rotated K_2SO_4 (*) pellets of products A ($\lambda_{exc.}$ = 514.5 nm), B and [Bu$_4$N][Ni(dmit)$_2$] ($\lambda_{exc.}$ = 488 nm); right of the dotted line (> 1200 cm^{-1}) are the ν(C=C) signals of the compounds

[Bu$_4$N][Ni(dmit)$_2$]. The spectrum of A (Figure 3) clearly shows a signal at $g = 2.06$ of the radical anion [Ni(dmit)$_2$]$^-$ and a very broad signal with its maximum at $g = 5.5$, as pointed out by an arrow, indicating that a Co^{II} species must be present in A. In the spectrum of B (Figure 4) however, this signal is absent and only the anion signal is visible, which is almost identical to the signal of [Bu$_4$N][Ni(dmit)$_2$]. When considering the intensity of the Co^{II} EPR signal of A, no quantitative conclusions concerning the Co^{II} concentration in A can be drawn, because the intensity of the, normally very broad, Co^{II} EPR signals is, among others, strongly influenced by the relaxation times, that can differ between Co^{II} compounds.[27]

The conclusions concerning the cation charge in A and B based on the EPR spectra are confirmed by the XAS results. The spectrum (Figure 5) of A resembles very much a high-spin Co^{II} spectrum, whereas the spectrum of B agrees with a pure low-spin Co^{III} spectrum.[26]

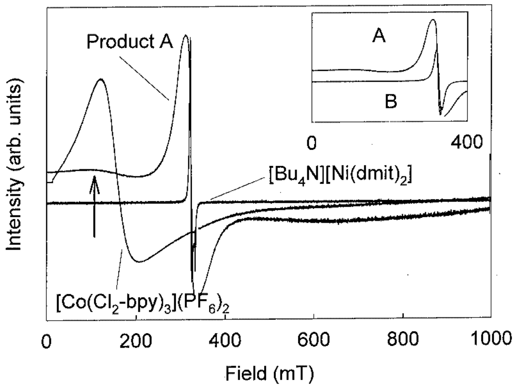


Figure 3. Powder sample EPR spectra at T = 77 K of [Bu$_4$N][Ni(dmit)$_2$], [Co(Cl$_2$-bpy)$_3$](PF$_6$)$_2$ and product A; the inset shows comparison of spectra of products A and B

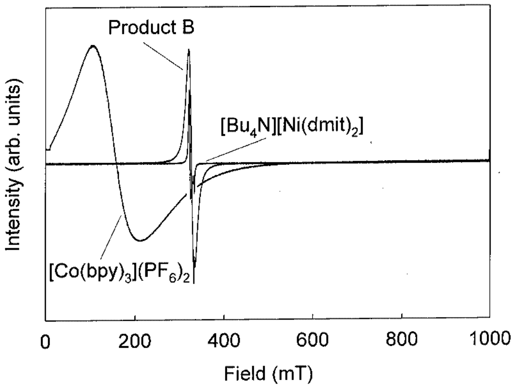


Figure 4. Powder sample EPR spectra at T = 77 K of [Bu$_4$N][Ni(dmit)$_2$], [Co(bpy)$_3$](PF$_6$)$_2$ and product B

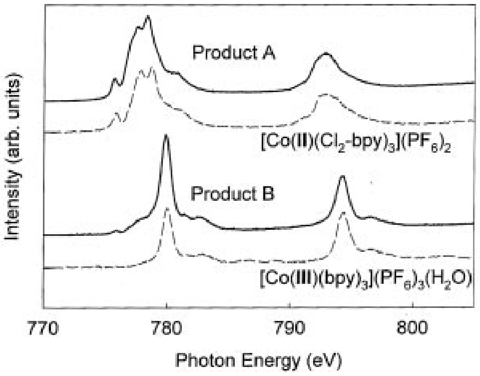


Figure 5. XAS spectra of A and B (——) and of [Co^{II}(Cl$_2$-bpy)$_3$](PF$_6$)$_2$ and [Co^{III}(bpy)$_3$](PF$_6$)$_3$(H$_2$O) (----) as reference compounds

Product B has a cation/anion ratio of 1:3, as indicated by elemental analysis. For product A this is somewhat more difficult to determine. The elemental analysis suggests a ratio of 1:5.4, whereas the AAS indicates a ratio 1:4.5. This discrepancy between the two results is significant, but may still be within the margin of error for compounds with non-integer stoichiometries, like many M(dmit)$_2$-based compounds. It is evident that the cation/anion ratio of A, which is assumed to be 1:5 here, is significantly lower than that of B, also, like the Raman results, implying the presence of Ni(dmit)$_2$ species with formal charge x ($0 < x < 1$) in A.

The room-temperature powder conductivities of A and B are both around $\sigma_{rt} = 2 \cdot 10^{-3}$ S/cm. This similarity is remarkable considering the differences in stoichiometry and Ni(dmit)$_2$ oxidation state of the two compounds; A was expected to have a higher conductivity than B. However, the two-point powder conductivity technique is quite inaccurate for determining the true intrinsic conductivity of a compound. Contact resistance and inter-grain electron hopping in the compressed powder pellet inhibit an accurate measurement. Only single-crystal conductivity measurements can give this true intrinsic conductivity of these compounds. Studies of the magnetic properties of these materials are in progress.

Further efforts to obtain single crystals and studies on combining other Co^{III}(N,N-imine)$_3$ complexes with M(dmit)$_2$ (M = Ni, Pd) are ongoing.

First findings show, that also for Pd(dmit)$_2$ anions the above described strategy is a successful one, resulting in compounds with a paramagnetic Co^{II} cation and Pd(dmit)$_2$ anions with a non-integer formal charge. More detailed studies are in progress.

Conclusion

In conclusion can be stated, that combination of the appropriate ($\Delta E > 0.1$ V) Co^{III}(N,N-imine)$_3$ complex with an M(dmit)$_2$ anion (M = Ni, Pd) allows the preparation of a partially oxidised, M(dmit)$_2$-based material, with a paramagnetic cation. Variation of the bis(imine) ligand enables fine tuning of the redox potential of the cobalt cation complex. In this way the oxidative power of the Co^{III} complex can be controlled.

In general can be concluded, that these Co^{III}(N,N-imine)$_3$ complexes can be combined with a great variety of different M(dithiolene)$_2$ anions with a suitable $E_{\mathrm{ox},1-/x-}$ oxidation wave potential. A large number of such anions is already known.[6] This strategy may give access to a whole new series of compounds, all consisting of a paramagnetic cobalt(II) cation and a partially oxidised bis(dithiolato)metallate.

Experimental Section

General Remarks: Resonance Raman spectra were recorded with a Dilor XY spectrometer using a Spectra Physics 2040E Ar+ laser as excitation source. Co $L_{2,3}$ XAS data were recorded in the Fluorescence Yield mode at the SRRC Dragon beamline. The electrochemical analyses have been performed using an Autolab PGSTAT10 potentiostat, Pt working and counter electrodes and an Ag/AgCl reference electrode.

[Bu$_4$N][Ni(dmit)$_2$]: This starting compound has been prepared according to the well-developed procedure first described by Steimecke[28] and modified by Lindqvist.[29]

[Co^{III}(X$_2$-bpy)$_3$](PF$_6$)$_3$·H$_2$O (X=H, Cl): The ligand 2,2′-bipyridine (bpy) is commercially available and has been used as received. The 4,4′-dichloro-2,2′-bipyridine ligand (Cl$_2$-bpy) has been synthesized according to a slightly adapted procedure described in the literature.[30] The two Co^{III} complexes have been prepared according to the literature.[31,32]

[Co(Cl$_2$-bpy)$_3$][Ni(dmit)$_2$]$_5$ (A) and [Co(bpy)$_3$][Ni(dmit)$_2$]$_3$ (B): The cation exchange reactions to obtain products A and B involve mixing of a 2 mM solution of [Bu$_4$N][Ni(dmit)$_2$] in acetone with a 2 mM [Co^{III}-(X$_2$-bpy)$_3$](PF$_6$)$_3$·H$_2$O solution in acetone, in a 3:1 molar ratio. The resulting black precipitates have been washed in acetone in an ultrasonic bath to wash out any enclosed starting compound, filtered off and dried under vacuum. A: Yield 50% with respect to [Bu$_4$N][Ni(dmit)$_2$]. IR (KBr): $\tilde{\nu}$ = 1654, 1560 (m, Cl$_2$-bpy), 1296 (m), 1246, 1058 (s, dmit), 922, 856, 827, 777, 747 (w, dmit), 667 (m, dmit), 497 (m, dmit) cm^{-1}. Elemental analysis found (calculated 1:5.4 cation/anion): C 22.56 (23.63), H 0.55 (0.57), N 2.53 (2.65), S 51.63 (54.59); calculated values with optimal C/N and S/N ratios. AAS found (calculated 1:4.5 cation/anion) Co 2.32 (2.17), Ni 10.25 (9.49); Co/Ni ratio 1:4.5. B: Yield 63% with respect to [Bu$_4$N][Ni(dmit)$_2$]. IR (KBr): $\tilde{\nu}$ = 1603, 1560 (w, bpy), 1446 (m, bpy), 1345, 1059 (s, dmit), 1025 (m, dmit), 920 (s, dmit), 757 (m, bpy), 511 (m, dmit) cm^{-1}. Elemental analysis found (calculated): C 30.29 (30.64), H 1.23 (1.29), N 4.51 (4.47), S 50.61 (51.12).

Acknowledgments

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