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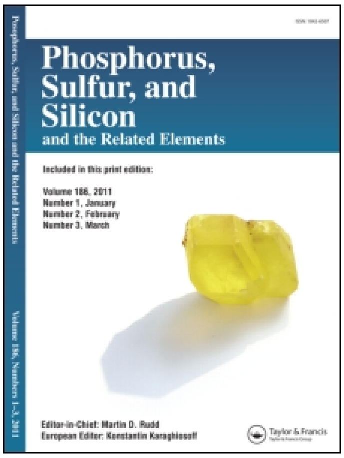

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New Bisdithiolene Metal Complexes of the 1,3-Dithiole-2-One-4,5-Dithiolate (Dmid) Ligand. Preparation, Characterization, and Electrochemical Properties

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NEW BISDITHIOLENE METAL COMPLEXES OF THE 1,3-DITHIOLE-2-ONE-4,5-DITHIOLATE (DMID) LIGAND. PREPARATION, CHARACTERIZATION, AND ELECTROCHEMICAL PROPERTIES

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The multi-sulfur donor ligand 1,3-dithole-2-one-4,5-dithiolate (DMID) has been prepared. Monoanionic or dianionic or non-integer oxidation state complexes of DMID with Ni(II), Cu(II) and Zn(II) have been isolated as the tetrabutylammonium (TBA), tetraethylammonium (TEA), or tetramethylammonium (TMA) salts. Elemental analyses give good results for all the compounds. In addition, the compounds are also characterized by negative ion Fast Atom Bombardment (FAB) mass spectral analysis, Fourier Transform Infrared spectral (FT-IR) analysis, UV-Vis spectral analysis and Cyclic voltammetry. Their electrochemical properties are studied.

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Key words: Bisdithiolene metal complex; multi-sulfur donor ligand; non-integer oxidation state complex; electrochemical properties.

INTRODUCTION

Metal complexes of sulfur ligands have been of interest for many years because of their applications in analytical chemistry, catalysis, and their relevance to bioinorganic systems.[1] Over the past decade, there has been renewed interest in metal complexes of sulfur-donor ligands for their unusual solid state properties (electrical,[1] magnetic,[2] and photoelectrical[3] properties etc.). Metal complexes of the DMIT(1,3-dithiole-2-thione-4,5-dithiolate) ligand have been important as a family of molecular conductors and superconductors.[4–8] These acceptor complexes are of interest due to their particular properties, and also to the many possibilities for chemical modification, such as changes in the chelating metal, and/or in the ligand itself, and/or in the countercation or donor molecule in the derived non-integer oxidation state or charge transfer compounds. Substituting selenium atoms for sulfur atoms in DMIT has led to a number of isologs of DMIT ligands.[9]

Recently, the polycrystalline thin film of the complex $[TBA]_2[Ni(DMIT)_2]$ exhibited electric field-induced switching and memory phenomena was reported.[10] In this paper, we present the preparation, characterization, and electrochemical properties of a series of tetraalkylammonium (TAA) salts derived from metal complexes of the oxo-bisdithiolene ligand DMID. These compounds are new complexes possessing optic and/or electric field-induced switching and/or memory system(s). Similarly, novel molecular metals or even superconductors derived from the metal complexes of the DMID ligand probably could be prepared.[11]

EXPERIMENTAL

Preparation of 1,3,4,6-tetrathiapentalene-2,5-dione, i.e. thiapendione, (4). A preliminary account of the synthesis of thiapendione has been given in a communication,[12] and a more detailed description of the preparation has also been reported.[13] The detailed conditions for each step which are important in terms of the yield of either the intermediate (3) or the thiapendione (4) have not been reported yet. A further more detailed description of the synthetic procedures will be published elsewhere.[14]

Preparation of 4,5-bis-(benzylthio)-1,3-dithiole-2-thione, i.e. (DMIT) (COPh)$_2$, (5). Precursor compound (DMIT) (COPh)$_2$ (5) was prepared according to the reported procedure.[15]

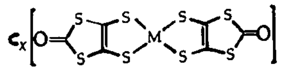
Preparation of 4,5-bis-(benzylthio)-1,3-dithiole-2-one, i.e. (DMID) (COPh)$_2$, (6). (DMID) (COPh)$_2$ (6) was prepared[16] in 1978 without a detailed description of the synthetic procedure. A more detailed description of the synthesis of 6 follows.

A boiling solution of mercuric acetate (10.4 g, 32.5 mmol) in 100 mL of glacial acetate acid was slowly added with stirring to a red solution of 5 (5.0 g, 13 mmol) in 400 mL of chloroform. After vigorous stirring for 15 min at room temperature, the white precipitate was filtered off and washed with chloroform (3 × 10 mL). The filtrate was washed with water (4 × 50 mL), and a red precipitate was filtered off and then washed with water again to neutralise any glacial acetate acid in the organic phase (chloroform). The solution was dried over MgSO$_4$ for a 1-h period. After filtration and removal of the solvent, a yellow crystalline solid was obtained. After recrystallization from chloroform/methanol (1:1), pale yellow needles of 6 were formed (3.6 g, 75% yield); m.p. 108.5–110.5°C. MS (EI, 70 ev) m/e 390. Found: C% 52.11 H% 2.33. Calcd for $C_{17}H_{10}S_4O_3$: C% 52.28 H% 2.58. FT-IR (KBr, cm^{-1}) spectra: 3056 (m) 1693 (s) 1667 (s) 1620 (m) 1577 (m) 1465 (m) 1445 (s) 1302 (m) 1202 (s) 1172 (m) 998 (s) 880 (s) 768 (s) 676 (s). UV-Vis (CH$_3$OH, λ_{max}) spectra: 248.7 nm. ^{1}H-NMR (200 MHz, CDCl$_3$, TMS) 7.45–7.98 (m, 10 H).

Preparation of Metal Complex [Ni(DMID)$_2$] [TMA] (TMA = tetramethylammonium), (8a). All reactions were carried out under argon unless otherwise stated.

TABLE I

Complexes of the type $[C]^x$ $[M(DMID)_2]$ i.e.



No.	C	x	M	Abbreviation
8a	TMA	1.0	Ni	$[Ni(dmid)_2][TMA]$
8b	TEA	1.1	Ni	$[Ni(dmid)_2][TEA]_{1.1}$
8c	TBA	1.0	Ni	$[Ni(dmid)_2][TBA]$
8d	TBA	1.1	Ni	$[Ni(dmid)_2][TBA]_{1.1}$
8e	TBA	1.2	Ni	$[Ni(dmid)_2][TBA]_{1.2}$
8f	TMA	1.0	Cu	$[Cu(dmid)_2][TMA]$
8g	TBA	1.1	Cu	$[Cu(dmid)_2][TBA]_{1.1}$
8h	TBA	2.0	Zn	$[Zn(dmid)_2][TBA]_2$

TMA: Tetramethylammonium, TEA: Tetraethylammonium

TBA: Tetrabutylammonium

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A 50-mL flask containing 10 mL of methanol and 207.8 mg (1 mmol) of thiapendione (4) was equipped with a dropping funnel which contained 15 mL of methanol and 5 mL methanol solution of sodium methoxide (0.43 M). The sodium methoxide solution was added dropwise to the flask at room temperature (30°C) with stirring for a 75-min period. The solution was stirred for another 25 min. To the brown-yellow solution was added a solution of $NiCl_2$ (120 mg, 0.5 mmol) in 10 mL of methanol with stirring for 2.5 hr, and then oxygen was bubbled through the reaction mixture for 30 min. After filtration, the dark green filtrate was treated with a solution of TMABr (617 mg, 4 mmol) in 10 mL of methanol with stirring for a 1-h period. A black precipitate was isolated by filtration, washed with methanol (4 × 5 mL), and air-dried. The crude complex was dissolved in 60 mL of acetone. After filtration, removal of the acetone gave a black crystalline powder $[Ni(DMID)_2]$ [TMA] (8a), which was collected by filtration with a minimal amount of methanol, washed with methanol (3 × 5 mL) and ether (3 × 10 mL), and then dried in air; yield 150 mg (60.8% based on 4). Found: C% 24.29; H% 2.48; N% 2.79. Calcd for $C_{10}H_{12}NS_8O_2Ni$: C% 24.34; H% 2.45; N% 2.83. Negative ion FAB mass spectrum: 418 $[Ni(DMID)_2]^-$. FT-IR spectra (KBr, cm^{-1}): 1682 (vs) 1614 (m) 1475 (m) 1408 (m) 1356 (s) 947 (m) 416 (m). UV-Vis spectra (methanol, λ_{max}, nm): 241.6, 310.4, 371.6.

Other complexes (8b, 8c, 8d, 8e, 8f, 8g and 8h) (see Table I) were prepared analogously.[15,17,18]

Elemental analysis were performed by the Analysis & Measurement Center of our institute with a Carlo Erba 1106 apparatus.

Infrared spectra were recorded on a Bruker IFS-113V Fourier Transform Infrared spectrophotometer in the region of 4000–400 cm^{-1} as KBr pellets.

UV-Vis spectrum was recorded by HITACHI 340 spectrophotometer in methanol solution.

Cyclic voltammetric measurements were performed with a EG & G PARC MODEL 175 UNIVERSAL PROGRAMMER and MODEL 174A POLAROGRAPHIC ANALYZER and MODEL RE0074 X-Y RECORDER at room temperature using dimethylformamide (DMF) solutions containing the $[M(DMID)_2][TAA]_x$ complex (2×10^{-3} M) and a supporting electrolyte (Et_4NBF_4, 0.1 M). A platinum disc (3 mm in diameter) was used as a working electrode. The counter electrode was a platinum plate which was immersed directly in the electrolyte solution. A saturated calomel electrode (SCE) was used as the reference electrode and also directly immersed in the electrolyte solution. Scan rate is 20 mv/s.

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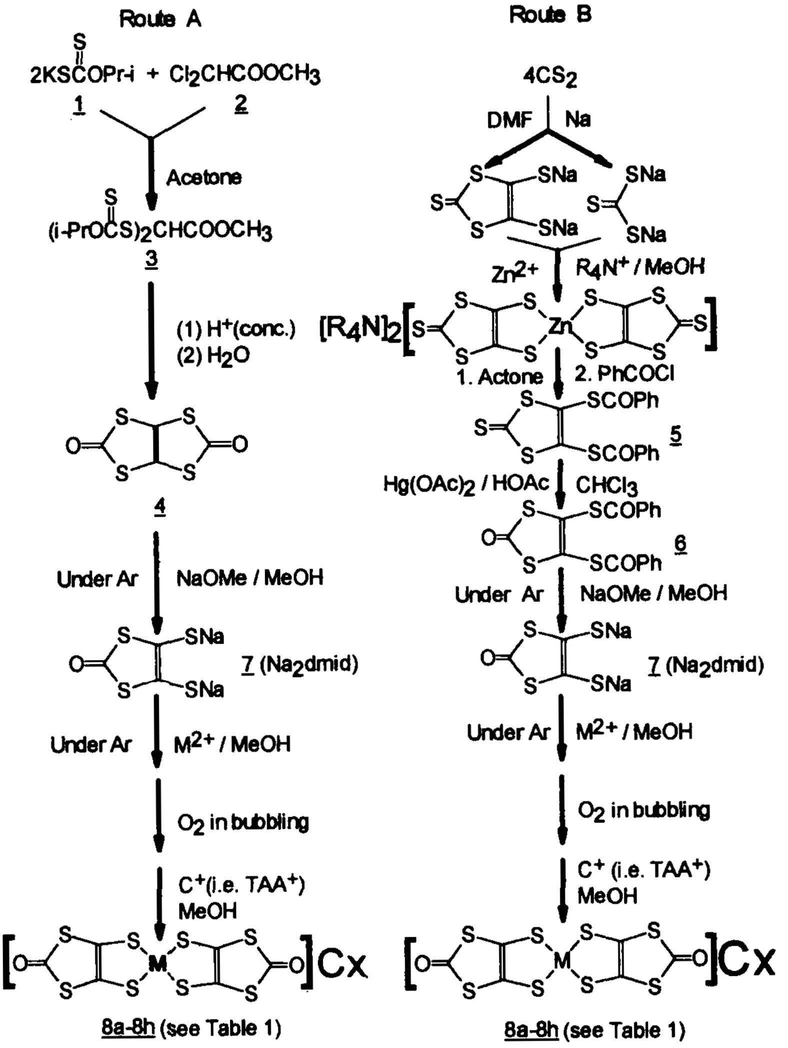
RESULTS AND DISCUSSION

Synthetic processes are shown in Scheme I. For the preparation of the ligand, two synthetic routes were studied. First (Route A), starting from 1,3,4,6-tetrathiapentalene-2,5-dione (thiapendione, 4), selective reaction of one of the carbonyl centers of thiapendione with base was used. Second (Route B), 4,5-bis-(benzylthio)-1,3-dithiole-2-one [(DMID) $(COPh)_2$, (6)] as the starting point, selective reaction of the benzyl centers of 4,5-bis-(benzylthio)-1,3-dithiole-2-one with base was used. Thiapendione or (DMID) $(COPh)_2$ under argon with 2 mol equiv of sodium methoxide in methanol at room temperature generated the air-sensitive dithiolate salts Na_2DMID, (7) (tetrathiolate salts also possible[11,15]) which were subsequently treated with a solution of $NiCl_2 \cdot 2H_2O$ or $CuCl_2 \cdot 6H_2O$ or $ZnCl_2$ in methanol, respectively, at room temperature under argon. After direct air-oxidation, addition of an excess of $n\text{-}Bu_4NBr$(TBABr) or Et_4NBr(TEABr) or Me_4NBr(TMABr) resulted in the precipitation of monoanionic or non-integer oxidation state species 8a–8g or dianionic specie 8h (without air-oxidation). Attempts to prepare the nickel and copper dianionic species in the same way (without aerial oxidation) resulted in dark green or dark blue oils which could not be purified and recrystallized.

Comparing the two synthetic routes (shown in Scheme I), Route B is better than Route A for the following reasons: The starting material, (DMID) $(COPh)_2$ in Route B can be obtained on a large scale in three days. Therefore, the succeeding synthesis can be done on a large scale, while, a large scale synthesis of the thiapendione is difficult and its yield is low. In addition, although thiapendione can



SCHEME I Synthetic procedures for the DMID ligand and related compounds.

be commercially obtained, it is very expensive. Furthermore, the thiapendione sensitizes and produces skin rashes on some individuals.

Elemental analyses gave good results for all of the compounds (see Table II). The yields changed from 60 to 78%, and all the integer oxidation state complexes were identified by the negative ion FAB mass spectrum which showed the molecular negative ion signal corresponding to the salt of the monoanionic or dianionic complexes. MS spectra: m^-/e 8a and 8c 418 $[Ni(DMID)_2]^-$, 8f 423 $[Cu(DMID)_2]^-$, 8h 425 $[Zn(DMID)_2]^{2-}$ and 667 $\{[Zn(DMID)_2]\ [TBA]\}^-$.

In Table III, the Infrared spectra (1700–400 cm^{-1}) of the complexes studied here are listed. All bands in this region can readily be assigned to the metal complexes of the DMID ligand (see Table III). The characteristic absorptions of the $C{=}O$, $C{=}C$, $C\overset{\cdots}{-}S$, $C{-}S$, and $M{-}S$ bonds in the bis(1,2-dithiolene) metal

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TABLE II
Elemental analyses Found (Calculated)

No.	Compound	C%	H%	N%
8a	$[Ni(dmid)_2][Me_4N]_{1.0}$	24.29 (24.34)	2.48 (2.45)	2.79 (2.83)
8b	$[Ni(dmid)_2][Et_4N]_{1.1}$	31.81 (31.59)	4.41 (3.94)	2.96 (2.74)
8c	$[Ni(dmid)_2][Bu_4N]_{1.0}$	40.27 (39.93)	5.71 (5.48)	2.07 (2.11)
8d	$[Ni(dmid)_2][Bu_4N]_{1.1}$	41.17 (41.32)	6.22 (5.82)	2.25 (2.25)
8e	$[Ni(dmid)_2][Bu_4N]_{1.2}$	42.62 (42.62)	6.29 (6.13)	2.46 (2.37)
8f	$[Cu(dmid)_2][Me_4N]_{1.0}$	23.81 (24.10)	2.37 (2.42)	3.02 (2.81)
8g	$[Cu(dmid)_2][Bu_4N]_{1.1}$	40.97 (41.03)	6.12 (5.78)	2.08 (2.23)
8h	$[Zn(dmid)_2][Bu_4N]_{2.0}$	49.92 (50.10)	7.94 (7.96)	2.95 (3.07)

TABLE III
Fourier Transform Infrared spectra (KBr disk, cm^{-1})

No.	C=O	C=C	C≃S	C-S	M-S
8a	1682 (vs)	1475 (w)	947 (m)	892 (w)	492 (w)
	1614 (m)	1408 (w)			416 (w)
8b	1670 (vs)	1468 (w)	980 (m)	888 (w)	484 (w)
	1610 (s)	1409 (w)			471 (m)
8c	1680 (vs)	1478 (w)	1070 (m)	883 (w)	448 (w)
	1618 (m)	1456 (w)			416 (w)
8d	1670 (s)	1409 (vw)	1027 (w)	900 (w)	471 (s)
	1612 (m)	1391 (vw)	980 (m)		425 (m)
8e	1670 (s)	1482 (w)	986 (m)	879 (w)	484 (s)
	1609 (m)	1450 (w)			
8f	1664 (m)	1456 (w)	949 (m)	892 (w)	486 (s)
	1601 (s)	1447 (w)			416 (m)
8g	1664 (s)	1456 (m)	992 (vw)	891 (w)	486 (w)
	1610 (s)	1410 (vw)			413 (m)
8h	1660 (s)	1465 (m)	1028 (m)	902 (s)	464 (s)
	1603 (vs)	1380 (m)	986 (s)	881 (w)	

vs: very strong, s: strong, m: middle, w: weak, vw: very weak

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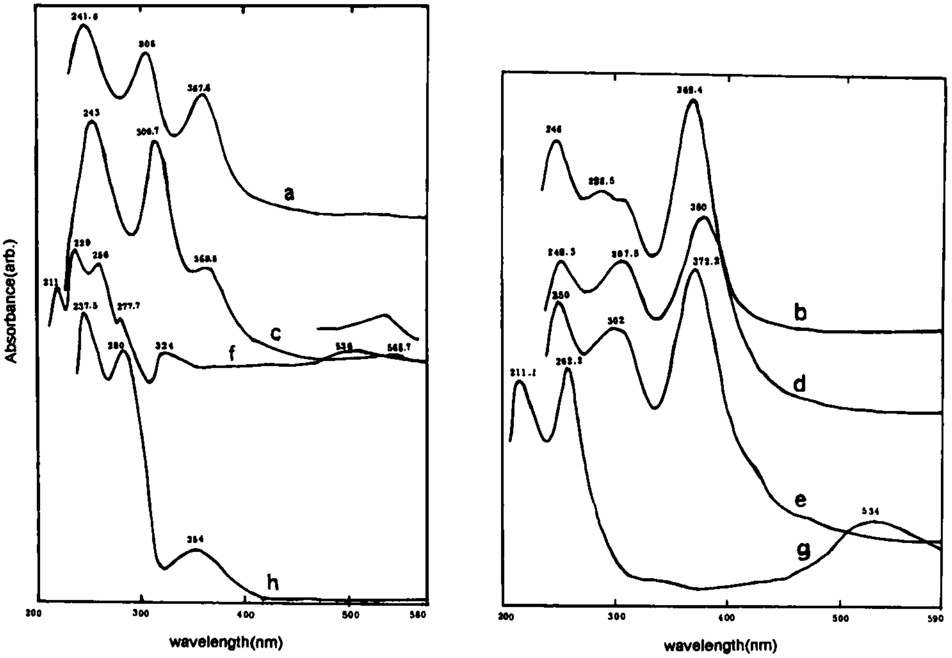

FIGURE 1 UV-Vis spectra of complexes 8a–8h (methanol).

complexes[15,19,20] lie within 1680–1600, 1490–1380, 1070–940, 910–880, and 490–410 cm^{-1} range, respectively. In the region 1230–1100 cm^{-1} appear two or three vibrational absorptions of the C—C single bonds of the alkyl group in the corresponding tetraalkylammonium ion.

The UV-Vis spectra data are shown in Figure 1. One of our interests for the study of UV-Vis spectrum comes from the π-electronic delocalization over the ligand which may be vital for the solid state properties of the metal complexes derived from them. The spectra of the related complexes show the characteristic bands of carbonyl group between 210–260 and 270–310 nm range, respectively,[20] and the obviously different absorbance between the integer and non-integer oxidation state Ni-chelating species 8a–8e at about 370–380 nm. The π-electronic delocalization absorption band over the ligand lie within 320–380 nm range. To the Cu-chelating complex 8g, this characteristic absorption is a very weak and broad one at about 330 nm (see Figure 1). This could be important evidence for the *d* electrons of the central metal ion to interact with the π electrons on the two ethylene double bonds through the lone-pair electrons on the inner four sulfide bridges, and the π electrons on the ethylene double bonds then interact with the π electrons on the carbonyl group through the lone-pair electrons on the outer four sulfide bridges.[20] Considering this kind of interaction between *d* and π electrons, we looked into the difference between the spectra of all Ni-chelating species 8a–8e and the Cu- or Zn-chelating species 8f–8h, we noticed that this characteristic band due to the π-electronic delocalization over the ligand through the central metal ion and the eight sulfide bridges blue-shifts from about 375 ± 5 nm in all Ni-chelating species to about 327 ± 3 nm and 354 nm in Cu-(8f–8g) and Zn-

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chelating (8h) species, respectively. This could be because the *d* electrons of d^7-configuration in Ni^{3+} or $Ni^{(3-\delta)+}$ more easily take part in conjugation than those of d^8- or d^{10}-configuration in Cu^{3+} (or $Cu^{(3-\delta)+}$) or Zn^{2+}, respectively. The red shift from about 327 ± 3 nm in the Cu-chelating species 8f–8g to 354 nm in the Zn-chelating specie 8h may be mainly due to the difference in valence state of the central metal ion and the amount of tetraalkylammonium ion in 8f–8g and 8h, respectively.

In Table IV, electrochemical data of the new complexes 8a–8h are listed. Complexes 8a–8g show two or more (three, four) irreversible oxidation peaks which could be tentatively assigned to the oxidation to (an) intermediate state(s) or finally

TABLE IV
Peak potentials of complexes 8a–8h (mv, vs SCE, 20 mv/s)

No.	Compound		Peak potentials				
8a	$[Ni(dmid)_2][TMA]_{1.0}$	Quasi-revers.	Eox	-215			
			Ered	-300			
		Irrevers.	Eox	430	760		
			Ered	310	150	-160	
8b	$[Ni(dmid)_2][TEA]_{1.1}$	Revers.	Eox	-520			
			Ered	-575			
		Irrevers.	Eox	320	750	1000	
			Ered	245	-100	-255	
8c	$[Ni(dmid)_2][TBA]_{1.0}$	Revers.	Eox	-200			
			Ered	-275			
		Irrevers.	Eox	520	700		
			Ered	300	-100		
8d	$[Ni(dmid)_2][TBA]_{1.1}$	Revers.	Eox	-550			
			Ered	-620			
		Irrevers.	Eox	360	1000		
			Ered	245	-275		
8e	$[Ni(dmid)_2][TBA]_{1.2}$	Revers.	Eox	-550			
			Ered	-620			
		Irrevers.	Eox	305	750	1000	
			Ered	215	-140	-270	
8f	$[Cu(dmid)_2][TMA]_{1.0}$	Irrevers.	Eox	300	540		
			Ered	-100	-800		
8g	$[Cu(dmid)_2][TBA]_{1.1}$	Revers.	Eox	-260			
			Ered	-280			
		Irrevers.	Eox	300	440	860	-50
			Ered	70	-60	-280	-800
8h	$[Zn(dmid)_2][TBA]_{2.0}$	Irrevers.	Eox	275			

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to neutral or partially anodic species. All Ni-chelating species 8a−8e show a reversible or quasi-reversible reduction peak between −620 and −275 mv which is assigned to the one-electron reduction from monoanion to dianion species.[20] Cyclic voltammograms show the obvious differences not only between the different chelating metal (Ni, Cu and Zn) complexes but also between the integer and non-integer oxidation state species.

According to the empirical rule stated by Wheland,[21] conducting charge-transfer complexes may be obtained when the difference between the half-wave potential of the donor and the half-wave potential of the acceptor lies between 0.1 and 0.4 V. Thus the [M(DMID)$_2$] complexes can be considered as acceptors and used in combination with appropriate donor molecules for preparing donor-acceptor complexes in which partial charge-transfer may be anticipated. More detailed descriptions of the electrochemical behavior of the complexes in terms of the guidelines for the preparation of conducting non-integral oxidation state complexes or charge-transfer complexes will be given in another paper in an extended form.

Studies on the possibility of optic and/or electric field-induced switching and/or memory effect(s) and on the potential molecular metals or even superconductors derived from the metal complexes of DMID are under way.

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