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The chemistry of 1,3-dithiole-2-thione-4,5-dithiolate (dmit)

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A. INTRODUCTION

One of the most remarkable developments in the border region between inorganic, organic and physical chemistry during the last decades is the fast and widespread increase in research in the field of coordination chemistry with unsaturated chalcogeno ligands. The area is derived from the 1,2-dichalcogenolenes, which are, for example, able to stabilize extended redox series of coordination compounds, generated in one-electron transfer steps without changes of the overall molecular symmetry (see refs. 1–11). Numerous papers deal with the electric or magnetic properties of such transition metal complexes and their use as organic metals. In addition to the metal chelates of 1,2-dicyano-ethylene-1,2-dithiolate (maleonitriledithiolate, mnt), first prepared by Bähr and Schleitzer in 1956 in Greifswald [12] (see, for example, ref. 13), complexes of the sulphur-rich 1,3-dithiole-2-thione-4,5-dithiolate (isotrithione-dithiolate, dmit), introduced by Steimecke (Leipzig, 1975) [14], are now the centre of attention (see, for example, refs. 15–19).

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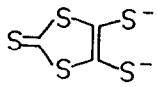


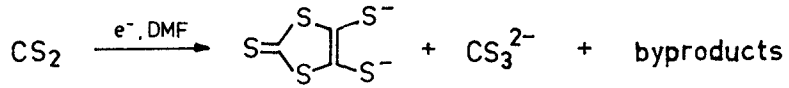
(1)

dmit

Meanwhile, derivatives of the "Steimecke compound" are available commercially (dibenzoyl derivative and zinc-chelate) [20]. Nowadays, transition metal bis-chelates of dmit are studied worldwide by numerous research groups. This was stimulated by those properties of the dmit chelates which favour electrical conductivity in molecular metals [21], e.g. planarity with delocalized π-electrons as well as open-shell character (dithiolene behaviour). These properties and the ready availability of the dmit ligand stimulated effective interdisciplinary studies in which chemists and physicists are involved. This review tries to compile "dmit chemistry", including inorganic and organic points of view. The literature is updated to approximately June 1990.

B. SYNTHESES OF 1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE (dmit)

1,3-Dithiole-2-thione-4,5-dithiolate (dmit) is formed as the main product by chemical [14,22] or electrochemical reduction [23(a)] of carbon disulphide in dimethylformamide (DMF).



(2)

dmit

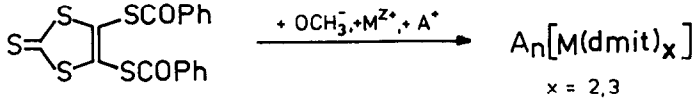
Large amounts of dmit can be prepared profitably by reduction of CS_2 using sodium or potassium [14,22]. The optimum solvent seems to be dimethylformamide even though the solvent itself reacts vigorously with the metals at ambient temperature. According to Steimecke et al. [14], the alkali metal should be added in portions to the boiling mixture of CS_2 and DMF and extreme caution is necessary to control the reaction safely. Otherwise, as reported, the reaction can proceed violently, even leading occasionally to explosions [24]. Moreover, the 1,3-dithiole-2-thione-4,5-dithiolate formed can rearrange into the isomeric 1,2-dithiole-3-thione-4,5-dithiolate (see Sect. E) at higher temperatures. Involving no risk, however, and according to Quante [22], the reaction between CS_2 and potassium in DMF proceeds readily under conditions of low temperatures, inert atmosphere and carefully dried DMF and CS_2. The dipotassium salt of 1,3-dithiole-2-thione-4,5-dithiolate (K_2dmit), isolated directly from the crude reaction product and described as unstable by Steimecke et al. [14], is also accessible by saponification of 4,5-di(benzoylthio)-1,3-dithiole-2-thione using a methanolic solution of potassium methanolate. It can be stored without decomposition for long periods at dry ice temperature in an inert gas atmosphere [25]. In addition to the electrochemical reduction of CS_2 in DMF

[23(a)], which is very suitable for producing small amounts of dmit, there are indications that the compound is also available by the classical Grignard reaction [26]. Several controversial views have been published about the mechanism of the reduction of CS_2. From the experimental facts one can suppose very complex reactions [cf. 23,27–31]. It is now proven and generally accepted that the initial step in the reduction of carbon disulphide is the formation of the radical monoanion $CS_2^{\cdot -}$. The crucial point then is whether a direct reductive coupling to tetrathiooxalate occurs [27,28(c)] from which, after reaction with excess CS_2 and expulsion of CS_3^{2-} and further electron uptake, dmit is formed (also explaining all the by-products), or whether carbon monosulphide (CS) is formed simultaneously with CS_3^{2-} which then react together in a different stoichiometry to form dmit [29]. The lithium [32(a)], sodium [33], ammonium [32(a)], tetraethylammonium [32(a)] and tetrabutylammonium [32(b)] salts of 1,3-dithiole-2-thione-4,5-dithiolate have also been described.

C. COORDINATION CHEMISTRY OF dmit

(i) Bis- and tris-chelates

The first metal chelates of 1,3-dithiole-2-thione-4,5-dithiolate were reported by Steimecke et al. in 1975 [14(a)]. The general method applied to synthesize dmit chelates is the solvolysis of the dibenzoyl compound $(PhCO)_2$dmit **1** by methanolic potassium or sodium methanolate followed by an in situ reaction of the generated dithiolate with the corresponding metal salt (eqn. (3)) [14(a)]. The anionic complexes formed can be isolated as crystalline salts using suitable large cations.



(3)

1

Numerous dmit chelates have been synthesized following that route. Besides variations of the metal ion and its oxidation state, they differ in the cation (A). Clearly, dmit complexes show "dithiolene" properties (different formal oxidation states of the central metal ion without remarkable structural change). Although dmit chelates of common metal ions are known, considerable interest has been focused on those of d^8 ions (nickel triad). The main research fields are the reversible one-electron transfer reactions of planar chelates as well as the creation of different arrangements of cations and anions in the molecular crystals, which cause a wide range of magnetic and especially electrical properties of the solids. Numerous chelate salts, mainly from $[Ni(dmit)_2]^{n-}$, have been synthesized with alkylammonium ions (see Table 1), sulphonium, sulphoxonium, phosphonium, arsonium, sodium, potassium ions (see Table 2), as well as sulphur- (selenium-, tellurium-) rich π-donors (see

TABLE 1

Alkylammonium salts of chelates of general formula $A_n[Ni(dmit)_2]_m$

A	n	m	Refs.
Me_4N	1	1	34, 35
Me_4N	1	2	36–38
Et_4N	1	1	35, 39, 40
Et_4N	1	2	39–41
Pr_4N	1	1	34, 35
Bu_4N	2	1	14, 42
Bu_4N	1	1	14, 35, 39, 43–48
Bu_4N	0.29	1	46, 49(a), 50(a)
Bu_4N	0.25	1	51(b), 51(c)
Bu_4N	0.20	1	51(a)
Me_3EtN	1	2	52(a)
Me_2Et_2N	1	2	38, 52
Me_2R_2N $R = C_nH_{2n+1}$ $n = 10, 12, 14, 16, 18, 22$	1	1	53
Me_3NH	0.5	1	49(b)
$Me_{4-y}NH_y$	n	1	49(b)

TABLE 2

Alkylsulphonium-, -sulphoxonium-, -phosphonium-, -(aryl)arsonium-, dithiolium-, dithiazolium-, and sodium- and potassium salts of chelates of general formula $A_n[Ni(dmit)_2]_m$

A	n	m	Refs.
Me_3S	1	2	52(a)
Me_3SO	1	2	52(a)
Me_4P	1	2	52(a)
Me_4As	1	2	52(a)
Ph_4As	0.25	1	16(d), 50(a), 56
dmt-Me_3[a]	0.5	1	57
dmt-Me_3[a]	2	1	58
dmt-Me_3[a]	1	1	58
$(PhNEt_2)$dta[b]	1	1	58
Na	0.35	1	51
K	0.4	1	59

[a] 3,4,5-Tris(methylthio)-1,2-dithiolium.

[b] 3-Diethylamino-5-phenyl-1,2,4-dithiazolium.

Table 3) as cationic constituents A. By combination of anionic bis-chelates of dmit (or dmt, see Table 12) as donors with methylviologen and similar bipyridinium cations as acceptors, intensely coloured ion pair charge-transfer complexes of type $Q[ML_2]$ are formed (see Table 4). Depending on the redox potentials of the constituents, they are semiconducting (in the solid state) and show IPCT bands in the long wavelength region (850–1250 nm) and short-lived photo-electron transfer [54(a)]. The neutral $[Ni(dmit)_2]$ (containing formally Ni(IV)) can also be prepared electrochemically and was characterized by X-ray crystal and molecular structure analysis, conductivity measurements and by cyclovoltammetry [46(b), 61(a)]. Only two species of the numerous nickel chelates listed in Tables 1–4 are superconductors, viz.

(a) the π-donor–π-acceptor complex $TTF[Ni(dmit)_2]_2$, first reported by Cassoux and coworkers [50,60,61], a 2D system with $T_c = 1.62$ K at 7 kbar, (10^5 S cm^{-1}) and

TABLE 3

Chelate salts with π-donors of general formula $A_n[Ni(dmit)_2]_m$

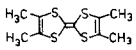
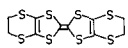
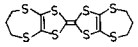
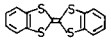
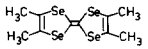
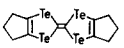
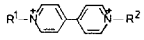
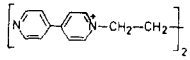
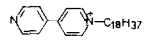
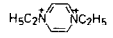
A	n	m	Refs.
TTF	1	1	32(b), 60
	1	2	16(b), 50(a), 60, 61
TMTTF	1	2	61(i)
			
BEDT-TTF (ET)	1	1	61(i), 62(a), (b)
	1	2	61(i)
BPDT-TTF (PT)	1	2	17(b), 62(b), (c)
			
EDT-TTF	1	1	38, 62(d)
	n	1	63
DB-TTF	1	1	17(a), (b), 62(b), (e)
			
TSF	1	3	64
			
TMTSF	1	1	17(a), 61(i), 62(b), 65(a)
			
HMTTeF	2	1	17(b)
			
$(Me_5Cp)_2Fe$	1	1	66

TABLE 4

Chelate salts with viologens of general formula $A_n[Ni(dmit)_2]_m$

A	n	m	Refs.
Viologen 			
MV $R^1 = R^2 = CH_3$	1	2	54
BV $R^1 = R^2 = C_4H_9$	1	2	54
OV $R^1 = R^2 = C_8H_{17}$	1	2	54
	2	1	54
StV $R^1 = R^2 = C_{18}H_{37}$	1	2	54
	2	1	54
EPSP $R^1 = C_2H_5$ $R^2 = C_3H_6SO_3^-$	1	1	54
DQ 	1	2	54
	2	1	54
MQ 	1	2	54
DP 	1	2	54
BBB 	1	2	54
StB 	1	1	54
DEPZ 	0.35	1	55

(b) the "closed-shell" cation/π-acceptor complex $Me_4N[Ni(dmit)_2]_2$ [36] with $T_c = 5$ K at 7 kbar (5×10^3 S cm^{-1}).

The α-phase of $TTF[Pd(dmit)_2]_2$ is also superconducting (see Table 5) [16(a), 50(a), 61(h)], whereas no Pt dmit chelates are yet known to show such behaviour (see Table 6).

Table 7 summarizes all other salts of bis-chelates (except those of the nickel triad) of dmit. In addition to the interest in conductivity (VO^{2+}, MoO^{2+}, Fe, Co, Rh, Cu, Au, see also ref. 86), their syntheses were also stimulated by indications of their potential use as pharmaceuticals claimed for radiopharmadiagnostica (Tc [70])

TABLE 5

Chelate salts of general formula $A_n[Pd(dmit)_2]_m$

A	n	m	Refs.
Me_4N	1	2	38
Me_4As	1	2	38
Et_4N	0.5	1	39(b), 40(a), (c), 48
Bu_4N	0.1	1	51(a)
Bu_4N	0.2–0.7	1	50(a)
Bu_4N	0.33; 0.5	1	50(b)
Bu_4N	1	1	14(c), 43, 51(b)
Bu_4N	2	1	14, 67(a)
dmt-Me_3[a]	0.5	1	57
$(PhNEt_2)$dta[a]	2	1	58
K	x	1	15(b), 59
Rb	x	1	15(b), 59
Cs	1	2	38
Cs	x	1	15(b), 59
DQ[b]	1	2	54
TTF[c]	1	2	16(a), (b), 50(a), 61(h)
TMTTF[c]	1	1	61(i)
BEDT-TTF[c]	1	1	67(b)
BPDT-TTF[c]	1	2	62(c)
TMTSF[c]	1	1	61(i)

[a] See Table 2.
[b] See Table 4.
[c] See Table 3.

or as cancerostatica (Ge [85])), in a photochemical context and photocatalysis (Ni, Pd, Zn, Cd, Hg [54,83,84]) and for NIR and FIR absorbing devices and materials, which do not absorb in the visible region (Ni, Cu, Co, Pd, Pt [87]). Additionally, $[Zn(dmit)_2]^{2-}$ is an excellent starting material for the preparation of organic derivatives of dmit (see Sect. D).

In the solid state, all known $[M(dmit)_2]^{n-}$ anions with M = Fe, Co, Rh, Ni (see Fig. 1, taken from ref. 44), Pd, Pt, Cu and Au are nearly square planar, irrespective of the oxidation state of the metal and no matter which cation is involved. As expected, the d^{10} metal ions Zn, Cd and Hg (see for instance ref. 82) are coordinated tetrahedrally. The first octahedral tris-complexes of dmit with V(IV), In(III) and Tl(III) were published in 1985 [25,69(a),88–90] (see Table 8).

The authors were interested in spectroscopic (e.g. EPR on V(IV) compounds) and structural data, as well as in the electrical conductivity of such non-planar dmit chelates in the solid state [69(a),89,90].

TABLE 6
Chelate salts of general formula $A_n[Pt(dmit)_2]_m$

A	n	m	Refs.
Bu_4N	0.2	1	51(b)
Bu_4N	0.26	1	17(b)
Bu_4N	0.3	1	51(a)
Bu_4N	1	1	14(c), 35, 43, 47, 50(a), 68
Bu_4N	2	1	14
dmt-Me_3[a]	0.5	1	57
DQ[b]	1	2	54
OV[b]	1	1	54(b)
TTF[c]	1	3	16(b), 50, 61(d)
DB-TTF[c]	1	1	62(b), (c)
HMTTeF[c]	3	1	62(b), 65(b)

[a] See Table 2.
[b] See Table 4.
[c] See Table 3.

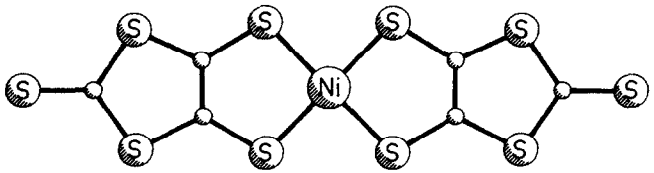


Fig. 1. Structure of $[Ni^{III}(dmit)_2]$ ions [44].

(ii) Mixed-ligand chelates

Generally bis- and tris-chelates of dmit are anionic (exceptions are, for example, $[Ni(dmit)_2]$ [61(a)] and $[Ge(dmit)_2]$ [85]), and the cation used is important for those solid state properties being described by the crystal structure (see Sect. C.(i)). Thus neutral mixed-ligand chelates of dmit in which there is interligand charge transfer and in which, simultaneously, the dithiolene properties are maintained, should be suitable for studies of both solid-state conductivity and spectral properties in solution. The compounds for this purpose include neutral mixed-ligand dmit chelates of Ni(II), Pd(II), Pt(II) and Ti(IV), anionic chelates of Ni(II), Cu(II), Zn(II) and Hg(II) and cationic chelates of Pd(III), Pt(III)/Pt(IV) (see Table 9). The methods applied were NMR, EPR, cyclovoltammetry, X-ray structure analysis, IR, UV/VIS and kinetic experiments. It is interesting to note that, so far, the expected high conductivities were found neither for neutral mixed-ligand dmit chelates nor for those doped with bromine or iodine.

TABLE 7
Chelate salts of general formula $A_n[M(dmit)_2]$

M	n	A	Refs.
VO^{2+}	2	Bu_4N	14(c)
	2	*N*-Methylpyridinium	69(a)
MoO^{2+}	2	Bu_4N	69(b)
	0.25; 0.15	Bu_4N	69(c)
	1	TTF[a]	69(c)
	2; 0.9	*N*-Methylacridinium (NMA)	69(c)
TcO^{3+}	1	Et_4N	70
Fe	1	Bu_4N	14(c), 45, 50(a), 71, 72
	0.028–0.05	Bu_4N	72(c)
	1	Pyrazine	72(a), (b)
	<1	Bipyridyl (bipy)	72(b)
	1	TTF[a]	72(a), (b)
Co	1	Bu_4N	14(c)
	0.3	Bu_4N	51(a)
Rh	1	Bu_4N	25, 73
	1.5; 0.4	Bu_4N	73
	0.25(Br); 0.35(I); $1((I_3)_{1.3})$; $1.5((I_3)_{0.4})$	Bu_4N	73
Cu	2	Bu_4N	14(a), (c), 74, 75
	1	Bu_4N	14(c)
	0.25	Bu_4N	51(a)
	2	Ph_4As	76
	2; $2(I_{2.5})$	*N*-Methylpyridinium	77
	2; $2(I_{2.9})$	*N*-Ethylpyridinium	77
	1.8	*N*-Methylphenazinium (NMP)	77
	1	DQ[b]	54(b)
	2	dmt-Me_3[c]	58
	0.5	TTF[a]	77
Au	1	Bu_4N	14(c), 43
	1	Pr_4N	78(a)
	1	Et_4N	79
	1	$(C_{10}H_{21})_3CH_3N$; R_2Me_2N	53(b), 80
	1	*N*-Methylpyridinium	78
	1	Me_3S	78(b)
	1	$(PhNEt_2)dta$[c]	58
	1.5	TTF[a]	81
	1.5	TMTSF[a]	81
	1	BEDT-TTF[a]	81
Zn	2	Bu_4N	14, 82, 83
	0.2	Bu_4N	51(a)

TABLE 7 (*continued*)

	2	Et_4N	14(d)
	1	Viologens (MV, OV, StV, DQ)[b]	84
	2	dmt-Me_3[c]	58
	2	$(PhNEt_2)$dta[c]	58
	1	Bu_4N/dmt-Me_3[c]	58
Cd	2	Bu_4N	14(c)
	1	Viologens (MV, OV, StV, DQ)[b]	84
	2	dmt-Me_3[c]	58
	2	$(PhNEt_2)$dta[c]	58
Hg	2	Bu_4N	23(b), 25
	1	Viologens (MV, OV, StV, DQ)[b]	84
	2	dmt-Me_3[c]	58
	2	$(PhNEt_2)$dta[c]	58
	1	Bu_4N/dmt-Me_3[c]	58
Ge	0		85
Se	2	Bu_4N	14(c)
	2	Ph_4As	25

[a]See Table 3.
[b]See Table 4.
[c]See Table 2.

TABLE 8

Tris-chelate salts of dmit of general formula $A_n[M(dmit)_3]_m$

M	*n*	*m*	A	Refs.
V	2	1	Bu_4N	25, 69(a), 88
	0.17	1	Bu_4N	69(a)
	2	1	*N*-Methylacridinium (NMA)	69(a)
	2	1	*N*-Methylphenanzinium (NMP)	69(a)
	2	1	TTF[a]	69(a)
	3	2	BEDT-TTF[a]	89
	1	1	Cp_2Ni	90
	1	1	$(Me_5Cp)_2Fe$	90
	1	2	Fe	90
	1	1	$Co(3H_2O)$	90
In	3	1	Ph_4As	25, 88
Tl	3	1	Ph_4As	25, 88

[a]See Table 3.

TABLE 9

Mixed-ligand chelates of general formulae $A_n[M(dmit)L]_m$ and $[M(dmit)L]_mX_n$

M	n	m	A, X	L	Refs.
Ni		1		$(CH_2PPh_2)_2$ (dppe)	91(a), (b)
		1		Bipyridyl (bipy)	91(c)
	1	1	Bu_4N	Et_2NCS_2 (Et_2dtc)	92
	1	1	Bu_4N	Et_2NCSSe (Et_2tsc)	92
	1	1	Bu_4N	Et_2NCSe_2 (Et_2dsc)	92
Pd		1		$(CH_2PPh_2)_2$ (dppe)	91(a), (b)
		1		Bipyridyl (bipy)	91(c)
	1	1	I	bipy	91(c)
		1		Phenanthroline (phen)	93
	1	1	I	phen	93
Pt		1		$(PPh_3)_2$	91(a), (b)
		1		$(CH_2PPh_2)_2$ (dppe)	91(a), (b)
		1		Bipyridyl (bipy)	91(c)
	1	1	Br	bipy	94(a)
	1	1	I	bipy	91(c)
		1		2,2′-Bipyrimidine (bipym)	94(b)
	1.6; 2.7	1	I	bipym	94(b)
		1		Phenanthroline (phen)	93
	1	1	I	phen	93
	1.9	1	I	phen	94(a)
		1		*N*-Ethyl-2-methyl-pyridine-2-carbaldimine (epa)	94(b)
	3.1	1	Br	epa	94(b)
	1.9; 3.4	1	I	epa	94(b)
Cu	1	1	Bu_4N	Et_2NCS_2 (Et_2dtc)	92
	1	1	Bu_4N	Et_2NCSSe (Et_2tsc)	92
	1	1	Bu_4N	Et_2NCSe_2 (Et_2dsc)	76, 92
Zn	1	1	Bu_4N	Et_2NCS_2 (Et_2dtc)	92
	1	1	Bu_4N	Et_2NCSe_2 (Et_2dsc)	92
Hg	2	1	Bu_4N	Br	84(a)
	1	2	Viologens (MV, DQ)[a]	Br	84(a)
	2	1	Bu_4N	I	84(a)
Ti	1	1		(Cyclopentadiene)$_2$ (Cp_2)	95, 96

[a]See Table 4.

[M(dmit)(dppe)] complexes [91] were used as starting materials for studies to explain the mechanism of conductivity in partially oxidized $(MC_2S_4^{x-})_n$ polymers [16(c)]. The background for the synthesis of $Cp_2Ti(dmit)$ was the expected anti-neoplastic effect known for other titanocene dithiolates (see, for instance, ref. 97), and

the use of the compound as a starting material for the synthesis of organic dmit derivatives (see Sect. D) [96]. Table 9 collects the mixed-ligand chelates containing one dmit ligand, and Fig. 2 (taken from ref. 91(b)) shows the structure of the complex [Pt(dmit)(dppe)].

D. ORGANIC DERIVATIVES OF dmit

There are two aspects which are essential for studying the organic chemistry of 1,3-dithiole-2-thione-4,5-dithiolate: 2-thioxo-, 2-oxo- and 2-selenoxo-1,3-dithiole and -1,3-diselenole are key precursors for the synthesis of tetrathiafulvalenes (TTF) or tetraselenafulvalenes (TSF) (see, for example, refs. 98–100). The charge-transfer complexes of the latter with electron acceptors (for example with tetracyanochinodimethane (TCNQ)) are often low-dimensional organic metals or semimetals (see, for example, refs. 101–114). The easy availability of dmit and its alkylation or acylation products enables a whole collection of substituted 1,3-dithiole-2-thiones [45,108,115–148] to be realized.

The synthesis of dmit is closely related to that of tetrathio-oxalate (tto). Drechsel and Kolbe succeeded as early as 1868 in Leipzig in the synthesis of oxalate by passing a stream of dry carbon dioxide over molten sodium [149]. In contrast to this, all experiments for generating tto by reductive dimerization of carbon disulphide failed until recently, yielding dmit as the main product instead of tto (see Sect. B). It was only in the 1980s that an authentic sample of tto was prepared [28(b),150]. However, in 1976, Hartke and his group had already synthesized the dimethylester of tto (**4**)

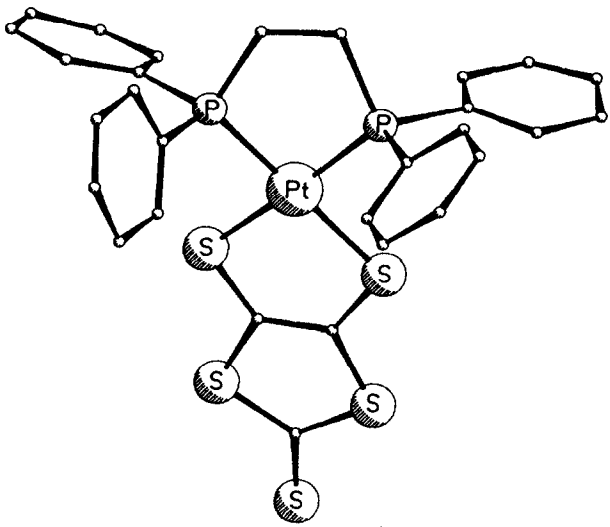
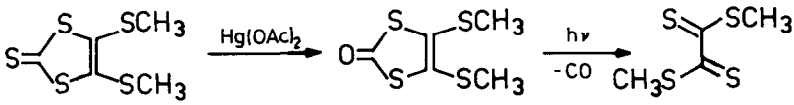


Fig. 2. Molecular structure of the mixed-ligand chelate Pt(dmit)(dppe) [91(b)].

[151] by photochemical decarbonylation of 4,5-dimethylthio-1,3-dithiole-2-one (**3**), which is formed by desulphurization of 4,5-dimethylthio-1,3-dithiole-2-thione (**2**).



(4)

2 *3* *4*

Some 50 years earlier, in 1927, Fetkenheuer et al. prepared **2** by reduction of CS_2 with sodium amalgam and subsequent methylation [152]. However, the authors believed that they had synthesized dimethyl-tetrathiooxalate (**4**). Nearly half a century later (1974–1976) three laboratories independently proved that Fetkenheuer had, in fact, isolated 4,5-dimethylthio-1,3-dithiole-2-thione (**2**) instead of dimethyl-tetrathiooxalate (**4**) [23(a),33,153] (see Table 10). Only the reduction of carbon disulphide with potassium or sodium in dimethylformamide, according to the procedure reported by Steimecke et al. in 1975 [14] or Quante in 1979 [22] (eqn. 2) and subsequent methylation gives optimum yields of **2**.

Three general synthetic routes have been found for the alkylation and acylation of dmit.

(1) In situ alkylation or acylation of dmit salts obtained by the electrochemical and/or chemical reduction of carbon disulphide (route A).

(2) Alkaline cleavage of 4,5-di(benzoylthio)-1,3-dithiole-2-thione and subsequent alkylation or acylation (route B).

(3) Reaction of $[Zn(dmit)_2]^{2-}$ with alkylating or acylating reagents (route C).

The dmit salts obtained primarily by the reduction of carbon disulphide are sensitive to air and moisture. Therefore, they must be transformed into stable and practicable compounds from which dmit can be recovered. 4,5-Di(benzoylthio)-1,3-dithiole-2-

TABLE 10

Methods for preparation of 4,5-di(methylthio)-1,3-dithiole-2-thione (**2**) by reduction of carbon disulphide followed by methylation

Reductant	Solvent	Yield of **2** (%)[a]	Refs.
Na/Hg		1.8	23(a), 33, 152,
Na	NH_3 (liq.)	2.1	33, 152, 153
Na	Naphthalene/THF	3.4	33, 154
Na	HMPT	3.8	33
e^-	DMF	12.2	23(a)
K or Na	DMF	70	14
K	DMF	95	22

[a]The yield calculation refers to the reductant used.

TABLE 11

Derivatives of 1,3-dithiole-2-thione-4,5-dithiolate dmit-R^1R^2

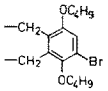
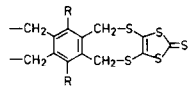
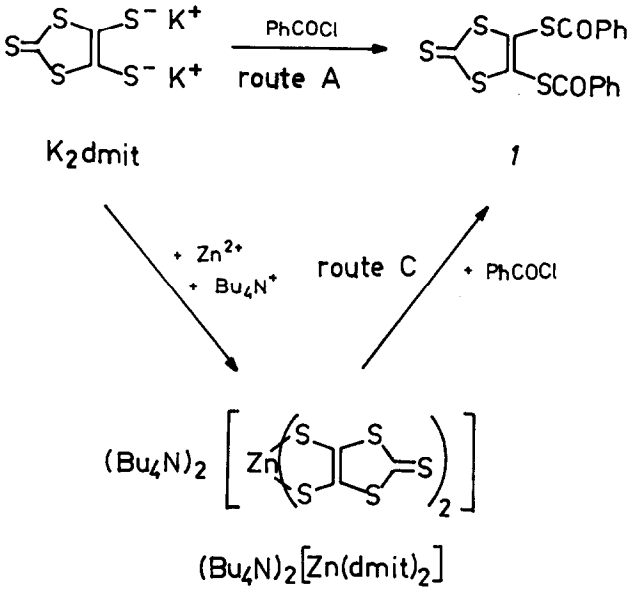
R^1	R^2	Route	Refs.
$-CH_3$	$-CH_3$ **2**	A	14, 22, 23(a), 33, 115, 151–153, 157
		B	14
		C	14
$-CH_3$	$-PO(OCH_3)_2$	C	96
$-C_2H_5$	$-C_2H_5$	B	156
		C	156
$-n\text{-}C_3H_7$	$-n\text{-}C_3H_7$	A	33
$-i\text{-}C_3H_7$	$-i\text{-}C_3H_7$	B	156
		C	156
$-CH_2-Ph$	$-CH_2-Ph$	B	14
$-CH_2COOH$	$-CH_2COOH$	C	14
$-CH_2COOCH_3$	$-CH_2COOCH_3$	C	158
$-(CH_2)_2-OH$	$-(CH_2)_2-OH$	C	159
$-(CH_2)_2-SCH_3$	$-(CH_2)_2-SCH_3$	A	160
$-(CH_2)_3-SCOCH_3$	$-(CH_2)_3-SCOCH_3$	A	160
		B	156
		C	156
$-CH(CH_3)-COCH_3$	$-CH(CH_3)-COCH_3$	B	161
$-CH(OC_2H_5)-CH_2Br$	$-CH(OC_2H_5)-CH_2Br$	C	161
$-CH(OOCCH_3)-CH_2Br$	$-CH(OOCCH_3)-CH_2Br$	C	161
$-COCH_3$	$-COCH_3$	C	14
$-COPh$	$-COPh$ **1**	A	155, 156
		C	14
$-CH_2-C\equiv CH$	$-CH_2-C\equiv CH$	C	162
$-CH_2-$		B	156
		C	156
$-CH_2-CH_2-$		A	14, 22, 163
		B	164
$-CD_2-CD_2-$		A	165
$-CH_2-CH_2-CH_2-$		A	22, 120
		B	164
$-CH_2-CH(CH_3)-$		C	158, 166
$-CH_2-CH(Ph)-$		B	148
$-CH_2-CH(C_{16}H_{33})-$		C	167
$-CH_2-CH(OC_2H_5)-$		C	161, 162
$-CH_2-CH(OOCCH_3)-$		C	161
$-CH_2-CH=CH-CH_2-$		A	168, 169
		C	147

TABLE 11 (*continued*)

	R = H R = OC_3H_7 R = OC_6H_{13}	C	147
	$-CH_2-CO-CH_2-$	C	170
	$-CH_2-S-CH_2-$	B	164
		C	170
	$-CH(CH_3)-CH(CH_3)-$	C	158, 166, 171, 172
	$-CH(CH_3)-(CH_3)C(OH)-$	B	161
	$-CH=CH-$	C	158, 162, 166, 173
	$-CH=C(CH_3)-$	C	162
	$-(CH_3OOC)C=C(COOCH_3)-$	C	96
	$>CH-COOCH_3$	C	174
	$>C=O$	A	45, 116, 119(a)
	$>C=S$	A	45, 116, 117
	$-S-$	A	160
	$-S-S-S-$	C	96

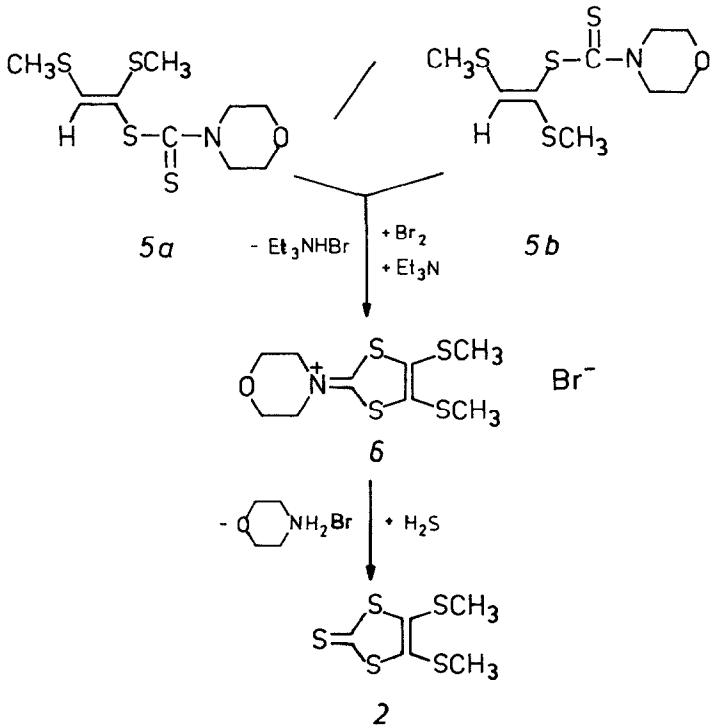
thione (**1**) (for X-ray structural analysis of **1** see ref. 155) as well as salts of $[Zn(dmit)_2]^{2-}$ are especially suited for this purpose. Steimecke et al. [14] favoured the synthesis of **1** by benzoylation of the zinc chelate (route C, eqn. (5)), whereas Köster [156] preferred the in situ acylation of the tetrabutylammonium salt ($(Bu_4N)_2$dmit, the product of the electrochemical reduction of CS_2) or of the potassium salt (K_2dmit, obtained by the chemical reduction of CS_2; route A).



(5)

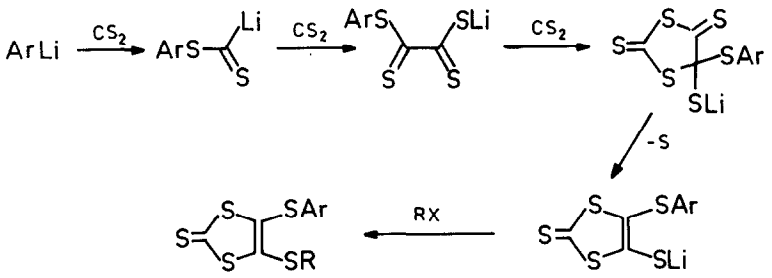
Table 11 collects dmit derivatives dmit-R^1R^2 and their syntheses (route A, B or C).

Another possibility for the synthesis of 4,5-di(alkylthio)-substituted 1,3-dithiole-2-thiones was described by Quante [22]. The cyclization of E/Z-(1,2-di(methylthio)-vinyl)-morpholino-dithiocarbamate **5a/5b** by bromine yields 4,5-di(methylthio)-2-morpholino-1,3-dithiolium-bromide (**6**) (eqn. (6)) in direct analogy to the procedure of Hiratani et al. [175] who obtained 2-dialkyl-amino-1,3-dithiolium-bromide by cyclization of S-vinyl-*N*,*N*-dialkyl-dithiocarbamates using bromine. Sulphurization of **6** with hydrogen sulphide in pyridine gives 4,5-di(methylthio)-1,3-dithiole-2-thione (**2**) in 78% yield. This cyclization reaction should be applicable to the synthesis of unsymmetrical alkylation products of dmit.



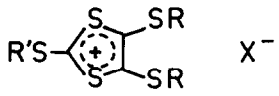
(6)

Unsymmetrically substituted 1,3-dithiole-2-thione-4,5-dithiolates can also be prepared by reaction of organolithium compounds (e.g. 2,4,6-tri-*tert.*-butylphenyllithium) with carbon disulphide [176]. An even greater palette of unsymmetrical substituted 4,5-dialkyl-halides-1,3-dithiole-2-thiones becomes available if homologous alkyl halides are used instead of that which is formed during the preparation of the aryllithium (e.g. 2,4,6.-tri-*tert.*-butylphenyl-lithium from 2,4,6.-tri-*tert.*-butylbromobenzene and *tert.*-butyllithium). However, the yields of this procedure are unsatisfactory [176]. The mechanism



(7)

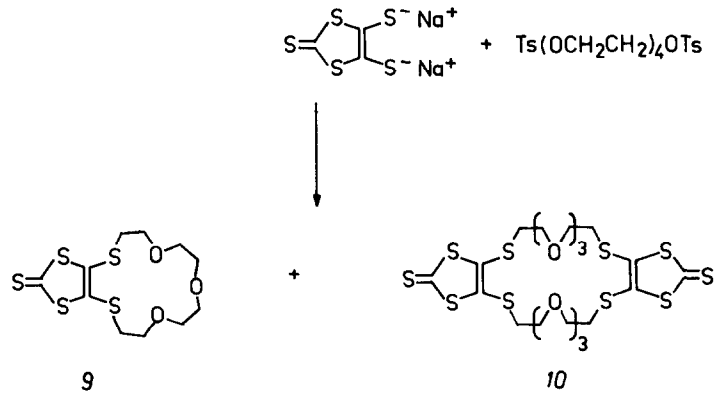
was proposed for this reaction. It is also possible to alkylate the thion sulphur of dmit derivatives by fluorosulphonic acid methyl ester or Meerwein's reagent. In this way, stable 1,3-dithiolium cations [22,177] (**8**) are available.



(8)

R' = CH_3, C_2H_5
R = See Table 11

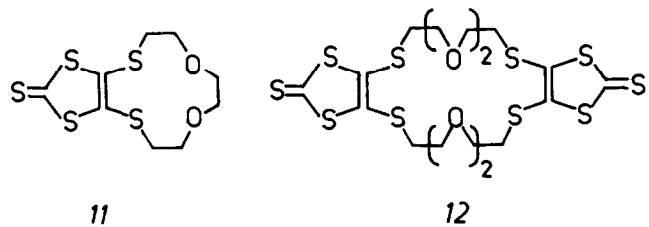
The first report of the synthesis of crown ethers with one or two dmit building blocks came from Otsubo and Ogura in 1985 [178] (**9** and **10**).



(9)

9 *10*

Higher yields of **9** and **10** were reached by Becher et al. [179] using the reaction of 1,11-dibromo-3,6,9-trioxaundecane with Na_2dmit at high dilution. The reaction of Na_2dmit with 1,8-dibromo-3,6-dioxaoctane [179] forms the macrocycles **11** and **12**.

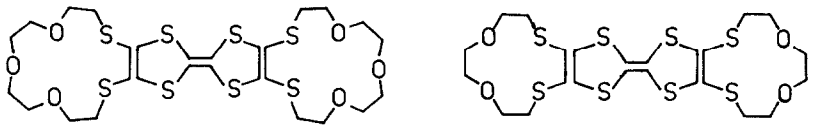


(10)

11 *12*

Crown ethers containing dmit building blocks are also accessible when starting from

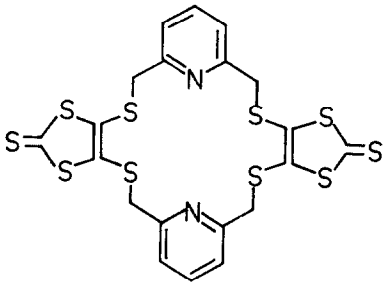
$[Zn(dmit)_2]^{2-}$ [180]. Like **9** and **11**, they are suitable for the synthesis of crown ether tetrathiafulvalenes [178–180] (see, for example, **13** and **14**) [178,179].



(11)

13 *14*

The macrocycle **15** can also be prepared from 2,6-dibromomethylpyridine and Na_2dmit [181].

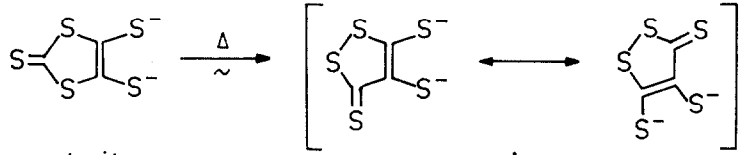


(12)

15

E. THE STEIMECKE REARRANGEMENT OF 1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE (dmit) INTO 1,2-DITHIOLE-3-THIONE-4,5-DITHIOLATE (dmt)

The 1,3-dithiole-2-thione-4,5-dithiolate salts formed by reduction of carbon disulphide in dimethylformamide (see Sect. B) rearrange in the same solvent at elevated temperatures into the isomeric 1,2-dithiole-3-thione-4,5-dithiolate (dmt) salts [14,182(a)] which are electronically more stable due to more extended electron delocalization (as depicted in eqn. (13) with two mesomeric VB-formulae).



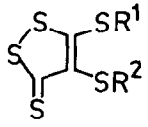
(13)

dmit dmt

HMO-calculations on 1,3-dithiole-2-thione-4,5-dithiolate and on 1,2-dithiole-3-thione-4,5-dithiolate confirm the greater delocalization energy of the latter ($\Delta E = 0.12836\ \beta$), i.e. the isotrithionedithiolate (dmit) to trithionedithiolate (dmt) rearrangement ("Steimecke rearrangement") is favoured as can be seen from the lowering of the total π-electron energy [183]. A proof that the "Steimecke rearrangement" proceeds without participation of by-products was provided in 1985 when the isola-

tion of potassium 1,3-dithiole-2-thione-4,5-dithiolate (K_2dmit) was successful for the first time [25]. The rearrangement depends on the solvent and also on the temperature. On heating K_2dmit for 4 h in acetonitrile or dimethylformamide at 80°C there is no rearrangement, whereas heating for 3 h in DMF at 100°C is sufficient for nearly complete conversion. Using HMPT as solvent requires 120°C but only 2 h. Only species of ionic dmit can be thermally rearranged. Obviously there is no such limitation if the reaction is initiated photochemically. Thus dmt-$(CH_2)_2$ is formed in this way from dmit-$(CH_2)_2$ (see Table 11) [184].

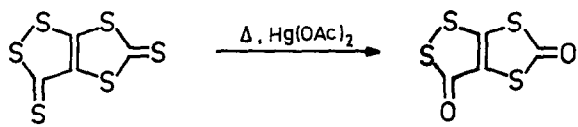
An alternative approach to dmt, according to Mayer and coworkers [185], involves the reaction of elementary sulphur with allyl halides in the presence of DMF. K_2dmt is stable and water-soluble and therefore suitable for alkylation and acylation. This is also true for the salts of its Zn- and Hg(II)-bis-chelates.



$R^1 = R^2 = H, CH_3, COPh$ [14c,182a]
$R^1 = Et_3NH^+, R^2 = COPh$ [14c,182a]
$R^1 = CH_3 \quad R^2 = COPh$ [14c,182a]
$R^1,R^2 = +CH_2+_n ; n = 1,2,3$ [186] (14)

4,5-Di(benzoylthio)-1,2-dithiole-3-thione, after solvolytic cleavage of the benzoyl groups, can also be used for the synthesis of further derivatives of dmt. 4,5-Di(methylthio)-1,2-dithiole-3-thione yields 3,4,5-tri(methylthio)-1,2-dithiolium iodide (dmt-Me_3I) [182] when methylated with CH_3I. (For ^{13}C-NMR sprectroscopic characterization of dmt derivatives see ref. 187).

The reactions of bifunctional alkylation or acylation reagents with dmt lead to condensed heterocycles. 1,2,5,7-Tetrathiapentalene-3,6-dithione (**16**), for instance, is available in good yield from $(Bu_4N)_2[Hg(dmt)_2]$ and thiophosgene [25]. It can be converted to 1,2,5,7-tetrathiapentalene-3,6-dione (**17**) by reaction with mercury(II) acetate [188].

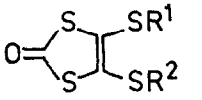


(15)

16 *17*

F. 1,3-DITHIOLE-2-ONE-4,5-DITHIOLATE (dmid)

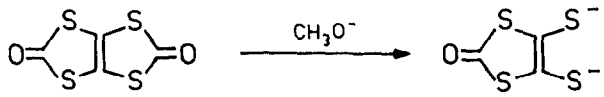
Transformation of the thiocarbonyl group in 1,3-dithiole-2-thione-4,5-dithiolate by mercury(II) acetate into a carbonyl group leads to 1,3-dithiole-2-one-4,5-dithiolate (dmid) [22,189], which is also an excellent chelating agent (see Sect. G.(ii)). Using this procedure, the majority of 1,3-dithiole-2-thione-4,5-dithiolate derivatives, listed in Table 11, yield the corresponding derivatives of dmid [22,156] without problems.



R^1R^2 = See Table 11 (16)

dmid-R^1R^2

Furthermore, dmid derivatives can be obtained by procedures already outlined in Sect. D for dmit: route A (from salts of dmid), route B (from 4,5-di(benzoylthio)-1,3-dithiole-2-one [156]), and route C (from salts of $[Zn(dmid)_2]^{2-}$ [156]). Another easily accessible precursor for dmid and its derivatives [123,126] is 1,3,4,6-tetrathiapentalene-2,5-dione (TPD) [116,117].



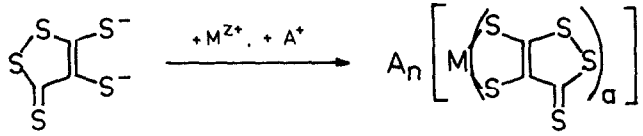
(17)

TPD dmid

G. COORDINATION COMPOUNDS OF dmt AND dmid

(i) Chelates of dmt

In direct analogy to dmit complex salts, those of the isomeric dmt can be prepared starting either from the dibenzoyl compound [14(c),182] or from stable salts of dmt, e.g. from the potassium (K_2dmt) [25,88,190], the tetraethyl [191], the tetrabutylammonium (yellow, f.p. 128–130°C) [192] or the tetraphenylarsonium (yellow, f.p. 154–156°C) salts [192].



(18)

dmt $A_n[M(dmt)_a]$

Chelate salts of dmt (see Table 12) are, as a rule, remarkably less soluble than their comparable dmit analogues (see Tables 1–8) in common solvents such as acetone, chloroform, pyridine, and dimethylsulphoxide. However, their tendency to crystallize is less pronounced. Planar bis-chelates of dmt (e.g. $(Bu_4N)_2[Ni(dmt)_2]$, see Fig. 3) obviously always contain the ligands in the "trans" position [182,187].

Mixed-ligand complexes of dmt are mainly known with Cu(II) and Zn(II) [76,84(a)] (see Table 13).

TABLE 12

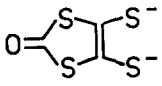
Chelate salts of 1,2-dithiole-3-thione-4,5-dithiolate (dmt) of general formula $A_n[M(dmt)_a]$

M	*a*	*n*	A	Refs.
Ni	2	2	Et_4N	48
	2	2	Bu_4N	14(c), 182
	2	1	Viologens (OV, DQ)[a]	54(b)
	2	2	dmt-Me_3[b]	58
	2	2	TTF[c]	193
	2	2	BEDT-TTF[c]	193
Pd	2	2	Me_4N	48
	2	2	Et_4N	48
	2	2	Pr_4N	48
	2	2	Bu_4N	14(c), 48, 182(a)
Pt	2	2	Et_4N	48
	2	2	Bu_4N	14(c), 182(a)
VO^{2+}	2	2	Bu_4N	14(c), 182(a)
V	3	2	Bu_4N	25, 88
Fe	2	1	Ph_4As	25
Co	2	1	Bu_4N	25
Cu	2	2	Et_4N	48
	2	2	Bu_4N	14(c), 182(a)
Au	2	1	Bu_4N	25
Zn	2	2	Bu_4N	25
Hg	2	2	Bu_4N	25
	2	2	dmt-Me_3[b]	58
	2	2	$(PhNEt_2)$dta[b]	58
Ga	2	1	Ph_4As	25
In	3	3	Ph_4As	25, 88
Tl	3	3	Ph_4As	25, 88
Se	2	2	Ph_4As	25, 194(a)
Te	2	2	Ph_4As	25, 194(b)

[a] See Table 4.
[b] See Table 2.
[c] See Table 3.

(ii) Chelates of dmid

Table 14 collects the bis-chelates of dmid reported in the literature.



(19)

dmid

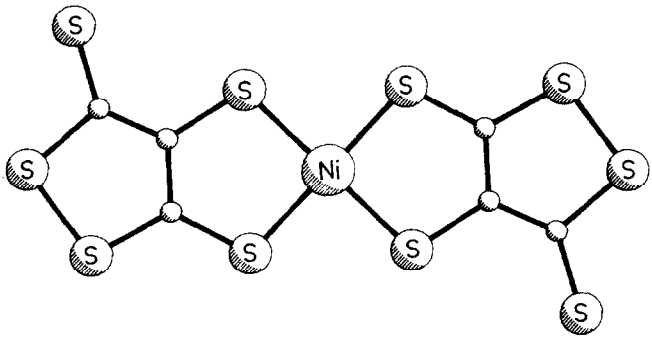


Fig. 3. Structure of $[Ni^{II}(dmt)_2]$ ion [182(b)].

TABLE 13

Mixed-ligand chelate salts of general formula $A_n[M(dmt)L]$

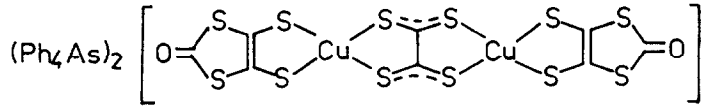
M	*n*	A	L	Refs.
Cu	1	Bu_4N	Et_2NCSe_2 (Et_2dsc)	76
Zn	2	Bu_4N	Cl_2	84(a)
	1	MV[a]	Cl_2	84(a)
	2	H	Cl_2	84(a)
	2	Bu_4N	mnt[b]	84(a)
	1	MV[a]	mnt[b]	84(a)

[a] See Table 4.

[b] mnt = maleonitriledithiolate ($^-S(CN)C{=}C(CN)S^-$).

4,5-Di(benzoylthio)-1,3-dithiole-2-one and 1,3,4,6-tetrathiapentalene-2,5-dione (TPD, see eqn. (17)) can be used as starting material for the in situ preparation.

Surprisingly, only the copper(II) compound $(Ph_4As)_2[Cu(dmid)_2]$ obtained from TPD converts into a C_2S_4-bridged dinuclear complex **18** in the presence of air in acetone/ethanol (1 : 1) [16(c),197(c)].



(20)

18

Mixed-ligand complexes of dmid containing Ni(II), Pd(II), Pt(II) and Hg(II) as central ions are also known (see Table 15).

A comparison of dmid chelates (see Tables 14 and 15) with those of the all-sulphur ligand dmit (see Tables 1–8) shows, despite their nearly identical coordination sphere and geometry, remarkable differences during the preparation of the com-

TABLE 14

Chelate salts of 1,3-dithiole-2-one-4,5-dithiolate (dmid) of general formula $A_n[M(dmid)_2]_m$

M	n	m	A	Refs.
Fe	1	1	Bu_4N	46
Ni	1	1	Me_4N	195
	2	1	Et_4N	48
	1	1	Bu_4N	196
	1.25	1	Bu_4N	195
	2	1	Bu_4N	196
	0.3	1	Ph_4As	197(a)
	1	1	Ph_4As	197
	2	1	Ph_4As	16(c)
	1	2	TTF[a]	197(a)
Pd	2	1	Et_4N	48
	1	1	Bu_4N	196
	2	1	Bu_4N	48, 196
Pt	2	1	Et_4N	48
	2	1	Bu_4N	48, 195
Cu	2	1	Et_4N	48
	2	1	Bu_4N	196
	2	1	Ph_4As	16(c)
Au	1	1	Ph_4As	16(c)
Zn	2	1	Me_4N	195
	2	1	Bu_4N	156(a)
Cd	2	1	Ph_4As	196
Hg	2	1	Bu_4N	196

[a] See Table 3.

TABLE 15

Mixed-ligand chelate salts of general formula $A_n[M(dmid)L_m]$

M	n	m	A	L	Refs.
Ni		1		dppe[a]	91(a)
Pd		1		dppe[a]	16(c), 91(a)
Pt		1		dppe[a]	91(a)
		2		PPh_3	91(a)
Hg	2	1	Bu_4N	mnt[b]	84(a)
	1	1	MV[c]	mnt[b]	84(a)
	1	1	OV[c]	mnt[b]	84(a)
	1	1	DQ[c]	mnt[b]	84(a)

[a] dppe = bis(1,2-diphenylphosphinoethane).
[b] See Table 13.
[c] See Table 4.

pounds. For instance, dmid complexes are more difficult to crystallize, melt at lower temperatures, and are oxidized more easily than their dmit analogues. Interestingly, the dmid complexes have a larger electron density between the carbon atoms of the double bond than do those of dmit (IR, ^{13}C-NMR [196]).

H. OUTLOOK

The various possibilities for the structural variation of complex salts of 1,3-dithiole-2-thione-4,5-dithiolate create a broad spectrum of interesting magnetic as well as electrical properties. The C_2S_5 unit can, for instance, be modified by partial or complete exchange of sulphur by selenium or tellurium. Thus, by reduction of CSe_2, it is possible to prepare 1,3-diselenole-2-selone-4,5-diselenolate (dsis) [198,199]. In 1986, the synthesis of 1,3-dithiole-2-thione-4,5-diselenolate (dsit) was reported by Nigrey [200]. As expected, the coordination chemistry of dsis and dsit shows similarities to that of dmit [88,201–203]. The route mentioned for the synthesis of dsit provides access to dmit analogues containing sulphur, selenium and/or tellurium. Until now, the following sulphur/selenium-containing analogues of dmit have been studied: 1,3-dithiole-2-selone-4,5-dithiolate (dmise) [204], and 1,3-dithiole-2-selone-4,5-diselenolate (dsise) [205].

NOTE ADDED IN PROOF

After submitting our manuscript, remarkably enough four comprehensive reviews on molecular metals and superconductors, based just on dmit and its selenium analogue dsis, were published by important contributors to the field [206–209]. In our opinion, this underlines the activity in the subject and we hope that our review will encourage new synthetic approaches in the chemistry and coordination chemistry of chalcogeno-rich ligands.

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