observed in the partially oxidized platinum chain salts ($M^{2.33+}$) and starch–iodine chain-type species (I_3^-), respectively.[7,24] Partially occupied electronic bands occurring in species of this type can produce metallic conduction.[7] Formulation (II) consists of stacked $M(DPG)_2^+$ units with I^- as the counteranion. Either metal d_{z^2} or ligand π bands will be half-filled in this model. Electronic spectra for $M(DPG)_2I$ (M = Ni, Pd) mulls (Figure 6) do not show the electronic spectral bands in the 6250-Å region characteristic of starch–iodine type materials,[24] which prompts us to favor formulation (II). However resolution of this problem must await complete X-ray structural characterization of these materials.

Acknowledgment. The authors acknowledge support of the National Science Foundation through Grant DMR72-03025 and Advanced Research Projects Agency Order 2380, Grant DAHC15-73-G14.

Registry No. $[Ni(DPG)_2(py)_2]I$, 53965-99-4; $[Ni(DPG)_2(py)_2]Br$, 53966-00-0; $Ni(DPG)_2$, 14286-61-4; $Co(DPG)_2(py)_2$, 42957-80-2; $Ni(DPG)_2I$, 53966-02-2; $Pd(DPG)_2I$, 53966-03-3; $Ni(DPG)_2Br$, 53966-01-1; $Pd(DPG)_2$, 16049-94-8.

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Thio Derivatives of 1,3-Diketones and Their Metal Complexes. Dithiomalonamide and Its Nickel(II), Palladium(II), and Platinum(II) Derivatives

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The complexes $[M(NH_2SacNH_2Sac)_2]$ (M = Ni, Pd, Pt; $NH_2SacNH_2Sac^-$ = dithiomalonamidate anion) have been synthesized and characterized. Comparative (ir, visible, uv, pmr, and mass) spectral studies on the divalent metal complexes and the related species dithiomalonamide and 3,5-diamino-1,2-dithiolium iodide have established their structural characteristics. The electrochemical behavior of the above compounds in acetone–0.1 *M* Et_4NClO_4 at both a dme and a platinum electrode is also reported. Polarography (dc and ac), coulometry, and linear sweep and cyclic voltammetry have been employed to investigate the electrode processes. The mass spectrometric behavior of a number of substituted 1,2-dithiolium cations is correlated in terms of pyrolytic decomposition as the precursor to ionization. It is concluded that NH_2SacNH_2Sac preferentially coordinates the group VIII metals *via* SS rather than SN or NN donation. The substitution of the CH_3 groups in dithioacetylacetone by NH_2 has been shown to have a marked effect on the redox and ion fragmentation behavior of these chelates.

Introduction

Dithiomalonamide[1] and N,N'-disubstituted dithiomalonamides[2] can function as either neutral or anionic ligands with nitrogen and sulfur available as potential donor atoms. The small amount of data available on such complexes[2–5] is conflicting and their interpretation is often speculative. Thus, bis(dithiomalonamidato)nickel is claimed to be dimeric in one report[3] and monomeric in another.[5] It has been inferred[4] that bis(dithiomalonamide)cobalt(II) dichloride coordinates *via* both sulfur atoms, while the coordination in the nickel analog is assigned[5] as being through sulfur and nitrogen. On the other hand, bis(dithiobiureto)nickel has been shown by X-ray analysis[6] to involve coordination *via* both sulfur atoms. Unfortunately, the interpretation of the infrared data obtained for some bis(dithiobiuret)metal(II) dichlorides is not compelling.[7,8] However, coordination *via* both sulfur atoms appears to be probable in these cases.

By contrast, complexes of dithioacetylacetone and related ligands have been more extensively studied.[9–15] Such studies have been hampered, to some extent, by the tendency of the free ligands to polymerize in the absence of a coordinating site. Oxidation of dithio-β-diketonate complexes frequently yields the corresponding 1,2-dithiolium ion.[10,16,17] Dithiomalonamide offers advantages over many dithio-β-diketones in that it is stable in the form of free dithiomalonamide and will complex metal centers as such. Alternatively, it can lose a proton and coordinate metal ions as an anionic ligand, or it can readily be oxidized to the "3,5-diamino-1,2-dithiolium" ion.[18] Hordvik[19] has suggested that this species would be better formulated as an imine-type moiety, and this is reflected in some of its chemistry (*vide infra*). However for purposes of reference and comparison, we will refer to it as a dithiolium ion.

The electrochemical behavior of tris(β-diketonato)ruthenium complexes has been shown to depend upon the nature of the chelate ring substituents,[20] and a similar effect has been observed with dithio-β-diketonates. In particular, the replacement of both CH_3 groups by NH_2 groups should facilitate oxidation of the derived metal complexes.

Accordingly, we have prepared complexes of both dithio-

Table I. Analytical Data

Compd	Mol wt		% C		% H		% N		% S		% M		% halogen	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$C_3H_6N_2S_2$			26.8	26.58	4.5	4.70	20.9	21.00	47.8	47.94				
$C_3H_5N_2S_2I$			13.85	13.99	1.94	2.10	10.77	10.51	24.65	24.56			48.79	48.69
$NiC_6H_{10}N_4S_4$	325	313	22.16	22.28	3.11	3.46	17.23	17.23	39.44	38.97	18.06	18.06		
$PdC_6H_{10}N_4S_4$	372	370	19.33	19.52	2.71	2.72	15.03	14.20	34.40	34.09	28.53	28.24		
$PtC_6H_{10}N_4S_4$[b]	462	[a]	15.61	16.00	2.18	2.31	12.14	11.44	27.79	27.45	42.27	39.13		
$NiC_4H_{10}N_6S_4$			14.68	14.92	2.47	2.50	25.70	25.92	39.21	39.44	17.95	17.75		
$NiC_6H_{12}N_4S_4Cl_2$			18.10	18.21	3.10	3.09	14.10	13.60	32.25	32.65	14.75	14.95	17.80	17.95

[a] Solubility in pyridine too low to obtain a reasonably accurate figure. [b] Calculated values for $PtC_6H_{10}N_4S_4 + {}^1/_8DMSO$ (see Experimental Section): C, 15.92%; H, 2.30%; N, 11.93%; S, 28.04%; Pt, 41.38%.

Table II. Infrared Data (cm^{-1})

3,5-Diamino-1,2-dithiolium cation[a]	Dithiomalonamide (LH)[b]	Assignment	NiL_2	PdL_2	PtL_2	Assignment
	3315	ν(N–H)	3420	3420	3410	ν(N–H)
	3270		3398	3398		
	3140		3280	3280	3280	
3280	2940	ν(C–H)	3180	3180	3180	
3140	2590	ν(S–H)				
1650	1622	$\delta(NH_2)$	1608	1608	1608	$\delta(NH_2)$
1625			1530	1525	1525	ν(C–N)
1530	1440	ν(C–N)	1435	1430	1428	
1515			1320	1320	1325	
1430	1290	ν(C–C)	1250	1245	1250	
1370	1220	$\nu(N\text{–}H) + \nu_{sym}(NCS)$				
1263			1130	1130	1130	
			1040			
1105	985	$\omega(NH_2)$				
	965					
	800	ν(C=S)	798	800	800	
			780	780	780	
	740	ν(N–H)	740	740	740	ν(N–H)
	720					
			655	655	650	
	615				615	
	600		585		590	
	530				565	
	460				490	
	420		450		450	
	405				400	
	290		320		350	

[a] As the chloride salt–ref 18. [b] Assignments from ref 4.

malonamide and the dithiomalonamidato anion with a view to comparing the related species: dithiolium ion, dithio-β-diketone, dithio-β-diketonate, and complexes of the latter two species. In particular, the new bis(dithiomalonamidato) complexes of palladium and platinum have been synthesized to complete the group VIII triad. Infrared, electronic, mass, and nuclear magnetic resonance spectra and polarographic behavior of all compounds have been reported in the hope of establishing the nature of the coordination and resolving anomalies in the literature.

Experimental Section

(a) **Syntheses.** Dithiomalonamide was prepared by the methods of Lehr, *et al.*[1] and of Schmidt.[21] 3,5-Diamino-1,2-dithiolium iodide was obtained by iodine oxidation of dithiomalonamide.[18]

Bis(malondithioamidato)nickel(II) $[Ni(NH_2SacNH_2Sac)_2]$. (For nomenclature, see ref 9 and 14.) A warmed aqueous solution of nickel acetate tetrahydrate (0.004 mol) was added to a stirred solution of dithiomalonamide (0.008 mol) in hot water. The dark green product separates immediately.

Bis(malondithioamidato)palladium(II) $[Pd(NH_2SacNH_2Sac)_2]$. A warmed aqueous solution of disodium tetrachloropalladate(II) (0.005 mol) was added to a stirred solution of dithiomalonamide (0.01 mol) and sodium acetate trihydrate (0.01 mol) in hot water. The orange product separates immediately.

Bis(malondithioamidato)platinum(II) $[Pt(NH_2SacNH_2Sac)_2]$. The mustard-colored product was prepared similarly to the palladium analog.

All complexes were recrystallized from dimethyl sulfoxide by the slow addition of methanol and dried at 0.05 Torr at 80° (yield 60–80%). However, repeated efforts failed to remove completely occluded solvent from $[Pt(NH_2SacNH_2Sac)_2]$.

Other complexes were prepared by published methods.[5,22] Analytical data are listed in Table I.

(b) **Instrumentation.** Instrumental techniques were as previously described,[11] with the following exceptions. Electronic spectra were recorded with a Cary Model 14 spectrophotometer, and mass spectra with MS-902 and CH-7 spectrometers. All elementary analyses and molecular weight estimations by vapor pressure osmometry were performed by the Australian National University Microanalytical Service.

Results and Discussion

(a) Dithiomalonamide (NH_2SacNH_2SacH). Since the initial synthesis by Lehr, *et al.*, very few references have been made to dithiomalonamide.[23] The infrared spectrum between 1650 and 700 cm^{-1} has been assigned by Jensen and Nielsen.[4] Table II lists those absorptions in the range 4000–200 cm^{-1}. The solid-state infrared spectrum (in a KBr matrix) exhibits a peak at 2590 cm^{-1} characteristic of the S–H stretch.[24] However, this band is not observed in the DMSO solution spectrum, indicating that dithiomalonamide exists in the

Table III. ^{1}H Nmr Spectral Details

Compd	δ,[a] ppm			
	CH_2	CH	NH_2	Solvent
NH_2SacNH_2SacH	4.01 (2)		2.68 (4)	Acetone-d_6
$[C_3H_5N_2S_2]^+I^-$		6.59	~8.9	Acetone-d_6
$Ni(NH_2SacNH_2$-$Sac)_2$		5.59 (1)	7.11 (4)	DMSO-d_6
$Pd(NH_2SacNH_2$-$Sac)_2$		5.59 (1)	7.22 (4)	DMSO-d_6
$Pt(NH_2SacNH_2$-$Sac)_2$ [b]		5.55 (1)	7.24 (4)	DMSO-d_6
$[Ni(NH_2SacNH_2$-$SacH)_2]Cl_2$	4.04 (2)		9.57 (4)	DMSO-d_6

[a] Figures in parentheses indicate relative integrated peak areas.
[b] No extra peaks were observed over the range $+20 \geqslant \delta \geqslant -10$ ppm.

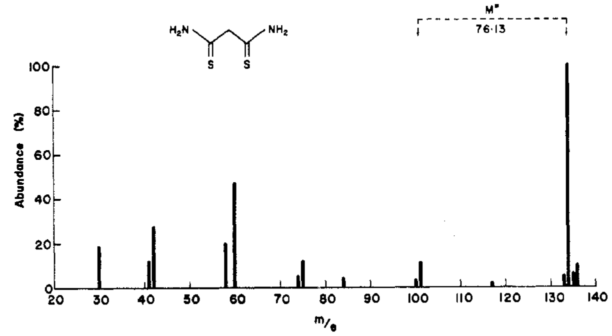
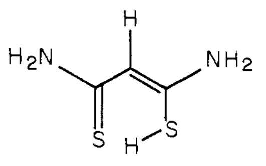
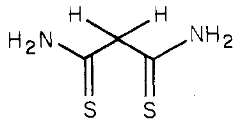


Figure 1. Mass spectrum of dithiomalonamide.

thio–enol form I in the solid state and probably as the dithione tautomer II in polar solvents.



I



II

This assignment is supported, in part, by our nmr studies in acetone-d_6 (Table III). Two peaks are observed at δ 4.01 and 2.67 ppm (relative to TMS) with integrated areas in the ratio 1:2, respectively. Kolesova, *et al.*,[25] reported the former peak and assigned it to the methylene protons. We assign the other peak to NH protons. Both peaks were observed to exchange with added D_2O with a resultant decrease in intensity. Dithiomalonamide may be compared with *O*-ethyl thioacetothioacetate (OEtSacSacH) which has been shown to exist in the thio–enol form in $CDCl_3$ solution.[14]

The mass spectrum of dithiomalonamide is reproduced in Figure 1. Peaks with an intensity <10% of the parent ion peak at *m/e* 134 have been omitted. The spectrum is dominated by the parent ion peak which is arbitrarily assigned an abundance of 100%. Interestingly, only a small peak is observed at *m/e* 133, corresponding to the 3,5-diamino-1,2-dithiolium cation, indicating very little decay *via* this species. In this respect, the behavior of dithiomalonamide contrasts with that of *O*-ethyl thioacetothioacetate[14] and of metal complexes of dithioacetylacetone.[9,11,12,26] A peak at *m/e* 101 and a metastable ion at *m/e* ~76 establish that the parent ion decays *via* loss of SH·

$$\underset{\text{mol wt }134}{NH_2SacNH_2SacH} \xrightarrow{-e} \underset{m/e\ 134}{P} \xrightarrow[m^*\ 76]{-SH\cdot} \underset{m/e\ 101}{(P-33)}$$

Dithiomalonamide exhibits complicated dc polarographic behavior at a dropping-mercury electrode (dme) in acetone. Waves corresponding to oxidation and reduction steps have been observed; both were analyzed by the standard plots of i_d *vs.* $h^{1/2}$ and log $[(i_d - i)/i]$ *vs.* E and by estimation of $E_{3/4} - E_{1/4}$. The reduction wave at −1.90 V *vs.* Ag–AgCl is quite complex and appears to involve a reversible process followed by a second wave incorporating a number of nonreversible steps. The complexity of the reduction process is reflected in the asymmetry of its ac polarographic wave.

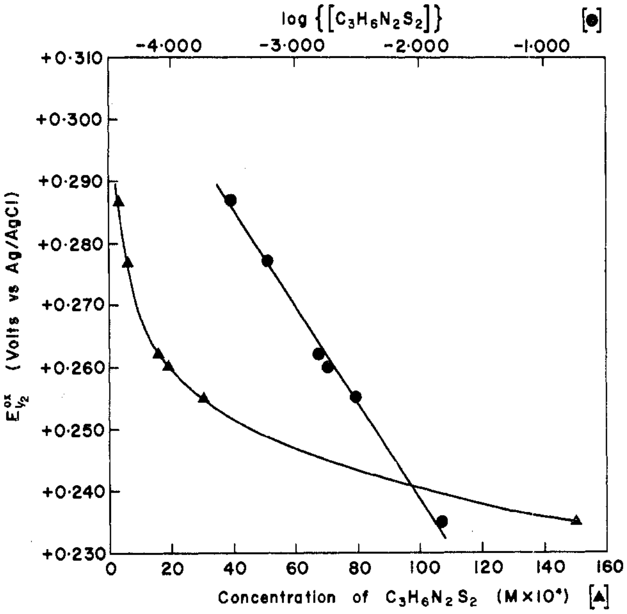


Figure 2. Concentration dependence of the dithiomalonamide oxidation wave.

In contrast, the oxidation step is apparently reversible and diffusion controlled. However, the potential at which the oxidation wave occurs is concentration dependent over the range 1.5×10^{-2}–3.0×10^{-4} *M*, yielding a value of approximately +0.32 V *vs.* Ag–AgCl at infinite dilution (Figure 2). Further, coulometry at a mercury pool shows that the oxidation requires 1.1 ± 0.1 electrons/mol of dithiomalonamide. Similar behavior has been observed in the polarography of *O*-ethyl thioacetothioacetate.[27]

The gross electrochemical behavior of dithiomalonamide, then, appears to be similar to that of *O*-ethyl thioacetothioacetate, although the lack of information about the electrochemistry of the possible products of the dithiomalonamide oxidation precludes a more detailed analysis and comparison with *O*-ethyl thioacetothioacetate.

However, should a ligand LH be oxidized by the generalized mechanism

$$Hg + nLH \rightarrow [HgL_n]^{2-n} + nH^+ + 2e^-$$

(as has been observed for *O*-ethyl thioacetothioacetate,[14] specifically with $n = 1$), then the Nernst equation requires that a plot of $E_{1/2}$ *vs.* log [LH] should be a straight line of gradient 60/2 mV at 25°. In the present case, such a plot is linear (Figure 2) and has a gradient of 31 mV (at 22°), implying the participation of 0.5 mol of dithiomalonamide per electron transferred in the oxidation (*i.e.*, $n = 1$).

The electronic spectrum of dithiomalonamide in Methyl Cellosolve has been reported previously.[5] Again, quite analogously to *O*-ethyl thioacetothioacetate,[14] we find the spectrum to be markedly solvent dependent.

(b) 3,5-Diamino-1,2-dithiolium Iodide. Hordvik's X-ray analysis[19] suggests that the cation should be represented by resonance structures such as IV, with the positive charge on the exocyclic nitrogen atoms, rather than by structures such

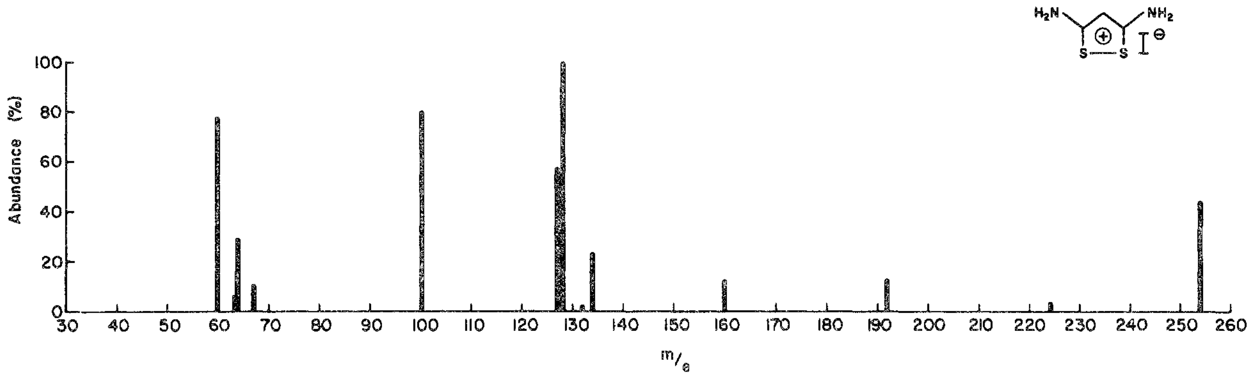
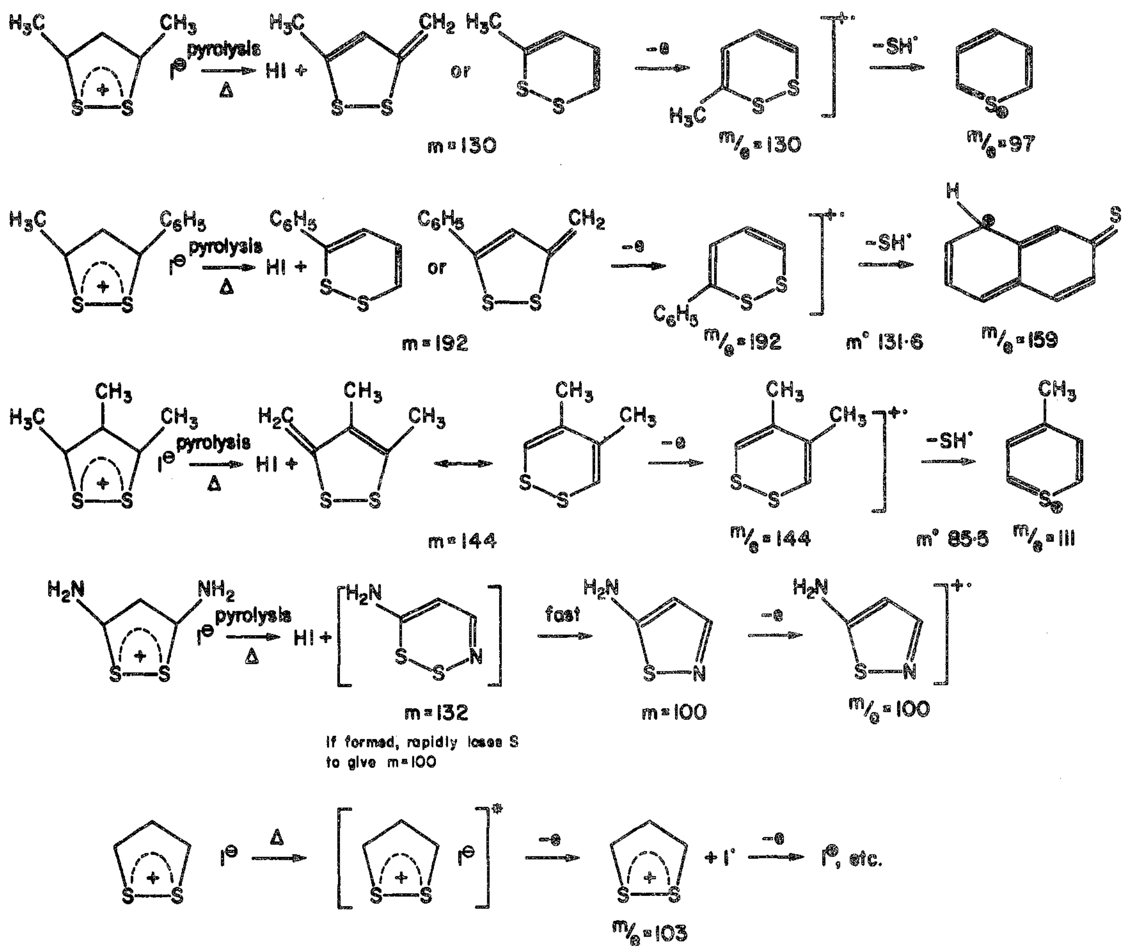
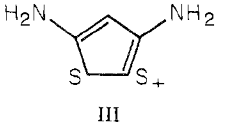


Figure 3. Mass spectrum of 3,5-diamino-1,2-dithiolium iodide.

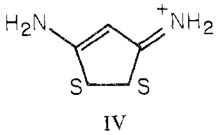
Scheme I. Mass Spectrometric Behavior of Some Substituted 1,2-Dithiolium Salts



as III, which are important for alkyl-substituted dithiolium cations.[28]



III



IV

Jensen[18] has reported the infrared spectrum over the range 4000–60 cm^{-1}, and these results are included in Table II for comparison. Kolesova, *et al.*,[25] have reported λ_{max} values in the electronic spectra of related N,N'-disubstituted 3,5-diamino-1,2-dithiolium ions in aqueous and alcoholic solutions. Thier values (λ_{max} ~300 nm, log $\epsilon \approx 4.5$) accord well with our values (λ_{max} = 291.8 nm, log ϵ = 3.71) for 3,5-diamino-1,2-dithiolium iodide in aqueous solution.

Voltammetric studies at a platinum electrode in acetone reveal (apart from an oxidation wave and a complex oxidation–reduction wave both attributable to the iodide ion) a nonreversible reduction at approximately −0.27 V *vs.* Ag–AgCl. This reduction is even more complex at the dme.

In an effort to characterize the mass spectrometric reactions of 3,5-diamino-1,2-dithiolium iodide (the mass spectrum of which is included in Figure 3), the iodide salts of a number of alkyl- and aryl-substituted dithiolium cations have been examined in the mass spectrometer.

The dithiolium iodides characteristically exhibit peaks at *m/e* 254, 128, 127, and 63.5 corresponding to I_2^+, HI^+, I^+, and I^{2+}, respectively. No parent ion is observed, but the spectra show strong (P − 1) peaks. These (P − 1) species then lose HS· to yield (P − 34) species, such loss generally being confirmed by the corresponding metastable ion peak.

These observations are consistent with pyrolysis of the dithiolium iodide in the mass spectrometer (this pyrolysis being accompanied by violent fluctuations of the ion currents) to yield neutral HI and (P − 1) species which then undergo electron-impact reactions as shown. Specific examples of this

$$\text{alkyl- or aryl-substituted 1,2-dithiolium iodide} \xrightarrow{\text{pyrolysis}}$$

$$\left\{\begin{array}{l} \mathrm{HI, I_2, etc.} \xrightarrow{-\mathrm{e}} \left\{\begin{array}{l}\mathrm{I_2}^+\\ \mathrm{HI}^+ \\ \mathrm{I}^+ \\ \mathrm{I}^{2+}\end{array}\right. \\ + \\ [\mathrm{P}-1]^0 \xrightarrow{-\mathrm{e}} [\mathrm{P}-1]^+ \xrightarrow[m^*]{-\mathrm{HS}\cdot} [\mathrm{P}-34]^+ \end{array}\right.$$

mechanism are included in Scheme I.

The parent 1,2-dithiolium iodide ($[\mathrm{C_3H_3S_2}]^+\mathrm{I}^-$) was the only exception to the above mechanism found in the present study. This salt yields the customary peaks due to the iodide ion and a *parent* ion peak. In this case, it is not unexpected that the salt sublimes (rather than pyrolyzing with loss of HI) to yield a complex activated species which then undergoes fragmentation to give the parent dithiolium cation and an iodine atom, this latter then undergoing the customary iodide reactions.

3,5-Diamino-1,2-dithiolium iodide would seem, at first sight, to disobey the above mechanism, there being only a small (P − 1) peak. However, it can still be thought to obey the general mechanism if it is assumed that the neutral (P − 1) species, if formed, rapidly loses sulfur to give a neutral (P − 33) species and that it is this (P − 33) species which undergoes the electron impact reaction giving rise to the peak at *m/e* 100. Low-intensity peaks due to formation and decay of $\mathrm{S_8}$ are also observed in the 3,5-diamino-1,2-dithiolium iodide mass spectrum.

The nmr spectrum of 3,5-diamino-1,2-dithiolium iodide in acetone-d_6 (Table III) shows a sharp resonance at δ 6.59 ppm attributable to the methine proton (this being in close agreement with that observed by Futterer in another solvent[28b]) and a broad resonance centered at about δ 8.95 ppm attributable to the $\mathrm{NH_2}$ protons. In contrast to the behavior of the $\mathrm{NH_2}$ protons in dithiomalonamide and in complexes of dithiomalonamide and of the dithiomalonamidiate anion, this latter peak is broad and poorly resolved.

(c) Metal–Dithiomalonamidato Complexes. The complexes with divalent nickel, palladium, and platinum are diamagnetic, appear to be quite air stable, and have melting points above 350°, with apparent decomposition above 200°. They are soluble in dimethyl sulfoxide, pyridine, dimethylformamide, and acetone but, unlike the corresponding SacSac compounds,[9] are insoluble, or only sparingly soluble, in chloroform and benzene. Molecular weight measurements establish that the nickel and palladium complexes are monomeric in pyridine. The similarity of the electronic and infrared spectra of the three compounds, coupled with the fact that the electronic spectrum of the nickel complex is the same in the solid state and in pyridine or dimethyl sulfoxide solutions, supports a monomeric nature for the three complexes. Odnoralova and Kudryavtsev's assignment[3] of the nickel compound as a dimer (on the basis of elemental analysis alone) is clearly erroneous.

The dithioacetylacetonates of divalent zinc,[29] nickel, palladium, platinum, and cobalt[9] all exhibit a parent ion in their mass spectra, with the most abundant peak occurring at *m/e* 131, corresponding to the 3,5-dimethyl-1,2-dithiolium cation.[9] The mass spectrometric behavior of the present compounds, however, differs greatly from that of the dithioacetylacetonates and from each other.

Figure 4 shows the mass spectrum of $\mathrm{Ni(NH_2SacNH_2Sac)_2}$. The principal differences from those of the divalent metal dithioacetylacetonates are the lack of a parent ion at *m/e* 325 (in fact, a lack of any substantial peaks at *m/e* values in excess of 136) and the lack of a large peak at *m/e* 133, corresponding to the 3,5-diamino-1,2-dithiolium cation.

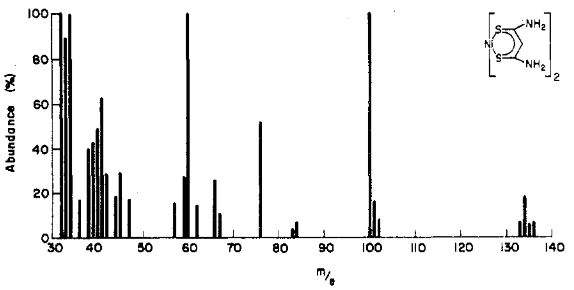


Figure 4. Mass spectrum of bis(dithiomalonamidato)nickel(II).

Scheme II[a]

$$\mathrm{M}^{n+}(\mathrm{SacSac})_n \xrightarrow{-\mathrm{e}} \underset{m/e\ 131}{\mathrm{C_5H_7S_2}^+} \xrightarrow[m^*\ 73.5]{-\mathrm{HS}} \underset{m/e\ 98}{(\mathrm{P}-33)}$$

$$\mathrm{M}^{n+} = \mathrm{Cr^{III}, Ni^{II}, Pd^{II}, Pt^{II}, Zn^{II}, Co^{II}}$$

$$\mathrm{Ni(NH_2SacNH_2Sac)_2} \xrightarrow{-\mathrm{e}} \underset{\substack{\text{not obsd}\\ m/e\ 133}}{\mathrm{C_3H_5N_2S_2}^+} \rightarrow \underset{m/e\ 134}{(\mathrm{P}+1)} \xrightarrow{-\mathrm{H_2S}} \underset{m/e\ 100}{(\mathrm{P}-33)}$$

$$\mathrm{Ni(CF_3SacSac)_2} \xrightarrow{-\mathrm{e}} \underset{m/e\ 185}{\mathrm{C_5H_4F_3S_2}^+} \left\{\begin{array}{l} \xrightarrow[m^*\ 149]{-\mathrm{F}\cdot} \underset{m/e\ 166}{(\mathrm{P}-19)} \\ \xrightarrow[m^*\ 125]{-\mathrm{HS}\cdot} \underset{m/e\ 152}{(\mathrm{P}-33)} \end{array}\right.$$

[a] The designation "P" applies only to the decay of the dithiolium ion and not to the dithio-β-diketonate complex.

A peak is observed at *m/e* 134, and apart from the lack of peaks corresponding to $\mathrm{S_8}$ decay, the mass spectrum of $[\mathrm{Ni(NH_2SacNH_2Sac)_2}]$ is very similar to that of the 3,5-diamino-1,2-dithiolium cation (*quod vide*) with peaks at *m/e* 134, 100, 84, 60, etc., suggesting that $\mathrm{Ni(NH_2SacNH_2Sac)_2}$ does, in fact, decay (perhaps thermally in the source) *via* the 3,5-diamino-1,2-dithiolium cation, as is observed with the divalent metal dithioacetylacetonates (Scheme II). However, the 3,5-diamino-1,2-dithiolium cation peak is not the most abundant peak in the mass spectrum of $\mathrm{Ni(NH_2SacNH_2Sac)_2}$, whereas the 3,5-dimethyl-1,2-dithiolium cation peak is the most abundant peak in the mass spectrum of the metal dithioacetylacetonates.

Perhaps the most interesting feature of the $\mathrm{Ni(NH_2SacNH_2Sac)_2}$ mass spectrum, however, is a weak but well-defined cluster of peaks about *m/e* 402. The position of this cluster and the isotope pattern suggest that it corresponds to $\mathrm{Ni(NH_2SacNH_2Sac)_2(DMSO)}^+$, *i.e.*, that a small amount of solvated complex has been volatilized and ionized complete with solvent DMSO.

The mass spectrometric behavior of $\mathrm{Pd(NH_2SacNH_2Sac)_2}$ is similar to that of its nickel congener, with respect to decay *via* the 3,5-diamino-1,2-dithiolium cation, but additionally it exhibits peaks at *m/e* 338 and 274, probably corresponding to loss of $\mathrm{H_2S}$ from the complex, followed by loss of $\mathrm{S_2}$ from the species so generated.

Corresponding additional peaks are not observed for $\mathrm{Pt(NH_2SacNH_2Sac)_2}$, but otherwise it behaves analogously to the nickel and palladium compounds, there being no parent ion nor $\mathrm{M(NH_2SacNH_2Sac)}^+$ peaks and decay *via* the 3,5-diamino-1,2-dithiolium cation being evidenced by peaks at *m/e* 134 and 100.

Table III summarizes the proton nuclear magnetic resonance spectra of the three compounds in DMSO-d_6. Two peaks are observed, with integrated areas in the ratio 4:1. The resonance at δ ~7.2 is slightly broadened. Its intensity is decreased upon addition of $\mathrm{D_2O}$ and, in the case of the nickel complex, this resonance is shifted to higher field on addition of DCl. The δ ~5.6 resonance is unchanged by these additions. Therefore,

Table IV. Pt–H Coupling Constants

Compd	*J*, Hz Pt–CH	Pt–CH_3	Pt–NH_2
$Pt(acac)_2$	11[a] 10.6[b]	5[a] 4.8[b]	
$Pt(SacSac)_2$	*d*	9[c]	
$Pt(OEtSacSac)_2$	6.2[e]	8.6[e]	
$Pt(NH_2SacNH_2Sac)_2$	2.3		6.9

[a] J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965). [b] P. J. McCarthy and A. E. Martell, *Inorg. Chem.*, **6**, 781 (1967). [c] Reference 31. [d] Not resolved due to limited solubility. [e] A. R. Hendrickson and R. L. Martin, *Inorg. Chem.*, **12**, 2582 (1973).

the former resonance is ascribed to the NH_2 protons and, as in dithiomalonamide, is observed despite ^{14}N quadrupole effects, presumably because of exchange with aqueous impurities in the solvent.[30] The latter resonance is assigned to the methine proton. In contrast to $Pt(SacSac)_2$,[31] the splittings due to the ^{195}Pt nucleus in $Pt(NH_2SacNH_2Sac)_2$ have been determined and are compared with those in analogous compounds in Table IV. Although J_{Pt-NH_2} is substantially larger than J_{Pt-CH} in $Pt(NH_2SacNH_2Sac)_2$, the significance of this is not clear.

Should the coordination of the ligand be *via* nitrogen rather than sulfur, a value of J_{Pt-NH_2} much larger than the observed value might be expected, Appleton and Hall[32] having reported values of J_{Pt-NH} of *ca.* 60 Hz for square-planar platinum(II) diamine-type complexes.

All the NH_2 protons of the title compounds have been found to be equivalent in the nmr experiment, such equivalence being suggestive of S,S or N,N chelation.

We have also found the NH_2 protons of $[Ni(NH_2SacNH_2SacH)_2]Cl_2$ to be equivalent in DMSO-d_6, although occurring at lower field than in $Ni(NH_2SacNH_2Sac)_2$ (Table III). Should the coordination in the chelated cation be S,N (as suggested by Peyronel, *et al.*,[5] on the basis of infrared peak splittings), then the equivalence of the amide protons would have to be ascribed to rapid exchange between the nonequivalent sites.

Accordingly, we have recorded the nmr spectrum of $[Ni(NH_2SacNH_2SacH)Cl_2$ in DMF-d_7 over the temperature range −80 to +35°. Although the spectra are extremely complex (possibly due to axial interaction of solvent with the compound leading to paramagnetism and its concomitant complexity), they are not consistent with a proton-exchange mechanism. The coordination in $[Ni(NH_2SacNH_2SacH)_2]Cl_2$ would thus appear to involve either N,N or S,S symmetrical chelation.

Table II incorporates the infrared spectral details of the present compounds. As a consequence of the four potential donor atoms of dithiomalonamide, there arises the possibility of S,S, N,N, or S,N chelation. The gross similarity of the spectra of the three compounds suggests that the ligands have the same conformation in all compounds. In assigning the mode of chelation, the infrared bands potentially of most value are those associated with metal–donor atom, C–S, C–N, and NH_2 vibrations.

Absorptions in the vicinity of 300–400 cm^{-1} in these compounds may reasonably be assigned to the metal–donor atom stretching mode. However, the possibility that these may be ring deformation modes cannot be ignored.[39] Although ν(M–N) bands seem to occur at higher frequency than analogous ν(M–S) absorptions, literature values of ν(M–N) and ν(M–S) show that these two regions overlap.[33–38] Accordingly, the metal–donor atom stretch cannot be used *a priori* for assigning the mode of coordination. Moreover, the coupling of the M–S stretch with other modes, as evidenced by normal-coordinate analyses[10,39,40] and the low intensities of these absorptions, militates further against their definitive use in this regard.

A shift of the dithiomalonamide ν(C–S) band to lower frequencies on chelation implies sulfur coordination.[4] However, normal-coordinate analyses on the divalent dithioacetylacetonates[10,39,40] show that the ν(C–S) vibration is strongly coupled to other modes (in $Co(SacSac)_2$, the 700-cm^{-1} band is calculated to contain 57% symmetric C–S stretch), and so such straightforward behavior of the C–S stretch may not necessarily occur. The use of this band for diagnosing the mode of chelation is further complicated by the fact that the C–S band in the complexes has been assigned as such because it is at lower frequency than in dithiomalonamide. Such an assignment requires the prior assumption of sulfur coordination and cannot therefore be used as proof of sulfur coordination.

Jensen and Nielsen[4] found that coordination *via* sulfur raises the N–H bending frequency, although they quoted exceptions to this generalization, one of which is $[Co(NH_2SacNH_2SacH)_2]Cl_2$, which they assumed to be sulfur chelated. A similar drop in the N–H bending frequency relative to dithiomalonamide is observed in the present compounds. However, the behavior of this band is not altogether straightforward, as in nickel dithiooxamide complexes,[41] where sulfur and nitrogen coordination occurs, the frequency of this absorption is consistently raised above the free ligand value.

An increase in the C–N stretching frequency in the complexes relative to dithiomalonamide would be consistent with sulfur chelation.[4] Such an increase is observed, but the ν(C–N) band of dithiomalonamide has been shown[4] to involve other coupled vibrations, although it is regarded as predominantly ν(C–N). Again, interpretations based on this band should be made cautiously and in conjunction with other evidence.

The bands of most importance in ascertaining the identities of the donor atoms are those associated with the N–H stretch (~3300 cm^{-1}). Normal-coordinate analyses on ligands containing a thioamide functional group have shown these vibrations to be substantially, if not completely, pure.[42,43] Several examples of ligands with nitrogen and sulfur as potential donors have been studied, and the N–H stretching vibrations have been used to establish the mode of coordination.[44–47] Coordination of $-NH_2$ groups to a metal ion has been shown to result in a shift of the N–H stretching absorptions to lower frequencies.[44,48,49] In the title compounds, the N–H stretching absorptions are at a slightly higher frequency than in dithiomalonamide, thereby implying sulfur coordination.

We believe, therefore, that the compounds involve sulfur-chelated ligands, such an assignment being based primarily on the position of the N–H stretch and supported by the shift in the C–N stretch. On this basis, it is then possible to assign the bands tentatively (Table II).

The electronic spectrum of $Ni(NH_2SacNH_2Sac)_2$ in dimethyl sulfoxide, in pyridine, and in the solid accords well with the values given by Peyronel.[5] Table V incorporates the electronic spectra of the present compounds. Their similarity to each other and to related compounds is apparent. As in the palladium and platinum compounds of OEtSacSac, low-energy bands corresponding to the d–d transitions of NiL_2 [L = SacSac, OEtSacSac, NH_2SacNH_2Sac] are not readily differentiated from the tail of the adjacent charge-transfer bands in the palladium and platinum complexes of NH_2SacNH_2Sac.

Electrochemical studies have been performed on the complexes in acetone at a dme and at a platinum electrode (Table VI). The compounds undergo both cathodic and anodic behavior at the dme.

Although in accord with the predictions of substituent effects

Table V. Electronic Spectra of Ni(II), Pd(II), and Pt(II) Complexes of NH_2SacNH_2Sac and of Related Ligands

$Ni(SacSac)_2$[a]		$Ni(OEtSacSac)_2$[b]		$Ni(NH_2SacNH_2Sac)_2$[c]		$Pd(NH_2SacNH_2Sac)_2$[c]		$Pt(NH_2SacNH_2Sac)_2$[c]	
ν, cm^{-1}	log ϵ	ν, cm^{-1}	log ϵ	ν, cm^{-1}	log ϵ	ν, cm^{-1}	log ϵ	ν, cm^{-1}	log ϵ
14,890	2.52	14,700	2.00	15,620	1.53				
		17,500	2.59	18,690	1.89				
18,120	3.45	20,600	3.66	24,100 sh	3.54	21,280	2.97	25,250	3.84
25,510	3.62	25,000	3.68	25,770 sh	3.89	27,470	3.51	29,760	4.28
29,670	4.33	29,300	4.40	31,250	4.56	33,080	4.07	32,470	4.47
35,460	4.59								
36,500	4.66	36,600	4.90	36,100	4.73	Not obsd		36,630	4.34
41,150	5.23	42,000	4.49	38,760	4.52	Not obsd		Not obsd	

[a] Reference 31. [b] A. R. Hendrickson, and R. L. Martin, *Inorg. Chem.*, **12**, 2582 (1973). [c] In DMSO solution.

Table VI. Polarographic Data[a]

Species	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$, mV	Gradient of log $[(i_d - i)/i]$ *vs.* E plot	n
NH_2SacNH_2SacH	$\simeq$+0.32[b]	33[b]	59[c]	1[d]
	−1.900	47	52	
Dithiobiuret	+0.448	50		
	−1.95	55		
$Ni(NH_2SacNH_2Sac)_2$	~+0.6	~28		
	−1.247	63	65	1
	−1.430			
	−1.760	46	42	
$Pd(NH_2SacNH_2Sac)_2$	+0.6	60		
	−1.482	85		
	−1.7			
$Pt(NH_2SacNH_2Sac)_2$	+0.640	63	75	
	−1.725	85		
	−1.980	80	0	

[a] Acetone as solvent; potentials *vs.* Ag–AgCl. [b] Extrapolated to infinite dilution. [c] At 1.0×10^{-3} *M*. [d] At 2.5 and 3.9×10^{-3} *M*.

that the reduction waves of the present compounds lie at far more negative potentials than those of the corresponding dithioacetylacetonates, the cathodic behavior remains similar to that of the dithioacetylacetonates, where the formal electron-transfer steps

$$\begin{tikzcd}
M(II) \arrow[r, "e^-"] & M(I) \arrow[r, "e^-"] \arrow[d, "k"] & M(0) \\
& {[M(I)]'} \arrow[r, "e^-"] & M(0)'
\end{tikzcd}$$

were observed.[50]

Similarly, three reduction waves were observed for $Ni(NH_2SacNH_2Sac)_2$, the first (most positive) of which was shown to be a one-electron process by coulometry at a mercury pool. Analyses of the usual type showed this first reduction to be diffusion controlled and reversible.

The second reduction wave (at $E_{1/2} = -1.430$ V) is very much smaller than either of the other reduction waves, and its height is dependent on drop time—the wave disappearing under rapid polarographic conditions.

Under normal polarographic conditions, the third wave was shown to approach reversible behavior, although analysis of this wave was complicated by the poor resolution of its current–voltage plateau, a consequence of the proximity of the cathodic limit of the solvent. The height of this third wave equaled that of the first wave under rapid polarographic conditions, while under normal conditions, the combined heights of the second and third waves nearly equaled that of the first wave.

Such behavior is consistent with the above reduction mechanism, with the rate constant, k, for the rearrangement of the first reduction product being smaller in the present case than for $Ni(SacSac)_2$.

Ac polarographic studies on $Ni(NH_2SacNH_2Sac)_2$ confirm a complication of the reduction pathway, as a plot of the peak current of the ac wave corresponding to the first reduction against the square root of the ac frequency ($10 < \omega < 1000$ Hz) is nonlinear.

The palladium and platinum complexes are reduced at potentials approaching the cathodic limit of the solvent and are therefore not as readily analyzed. Further, the reduction waves of these compounds are more complicated and the desired comparison with the corresponding dithioacetylacetonates is thus not possible.

Interestingly, although dithiomalonamide and dithiobiuret have similar redox potentials at the dme, reductions of bis(dithiobiureto)nickel(II) occur at more positive potentials than those of $Ni(NH_2SacNH_2Sac)_2$. [For bis(dithiobiureto)nickel(II), a small prewave at $E_{1/2} \simeq -0.96$ V, followed by two nearly overlapping waves of approximately equal height with $E_{1/2} \simeq -1.08$ and -1.17 V, is observed. A further reduction occurs at $E_{1/2} \simeq -1.91$ V *vs.* Ag–AgCl.] Even so, the electrochemical behavior of bis(dithiobiureto)nickel(II) is qualitatively the same as that of $Ni(SacSac)_2$ and of $Ni(NH_2SacNH_2Sac)_2$.

It might be anticipated that protonation of the amine function(s) of $Ni(NH_2SacNH_2Sac)_2$ should shift the reduction waves anodically, due to the differing effects of $-NH_2$ and $-NH_3^+$ upon the chelate ring. Accordingly, the titration of $Ni(NH_2SacNH_2Sac)_2$ and HBF_4 was followed polarographically.

A decrease in the height of the $Ni(NH_2SacNH_2Sac)_2$ reduction waves and the concomitant growth of an oxidation wave indicate that the metathetic reaction

$$Ni(NH_2SacNH_2Sac)_2 + 2HBF_4 \rightarrow 2NH_2SacNH_2SacH + Ni(BF_4)_2$$

occurs rather than protonation of the amine function on the intact complex. Confirmation of NH_2SacNH_2SacH as a reaction product was effected by performing the experiment in the presence of NH_2SacNH_2SacH and observing a growth and cathodic shift of the NH_2SacNH_2SacH oxidation wave.

All compounds exhibit an oxidation wave near +0.6 V (bis(dithiobiureto)nickel(II) also exhibits an oxidation wave, the potential of which is slightly more anodic). The proximity of these waves to the anodic limit of mercury prevents detailed analysis of such waves at the dme. However, cyclic voltammetric studies reveal that the oxidation process is complex and nonreversible at a platinum electrode. The shapes of the cyclic voltammograms seem to indicate coupling of the charge-transfer step to one or more chemical reactions, and the nonreversibility of the oxidation process may be attributable to these reactions, rather than to the charge-transfer step itself. Although oxidation of a ligand to the 3,5-diamino-1,2-dithiolium cation would explain the lack of reversibility, no evidence of this species is found on the cathodic sweep.

Further, the near equality of the dc pulse voltammetric oxidation and reduction wave heights of $Ni(NH_2SacNH_2Sac)_2$ at a platinum electrode suggests that both may be associated with the transfer of one electron. Formation of the 3,5-diamino-1,2-dithiolium cation would require the transfer of two electrons per $M(NH_2SacNH_2Sac)_2$ unit, *i.e.*

$$M^{II}(NH_2SacNH_2Sac)_2 \nrightarrow M^{II}(NH_2SacNH_2Sac)^+ + C_3H_5N_2S_2^+ + 2e^-$$

Thus it seems more likely that the voltammetric oxidation may involve the formation of a Ni(III) species, followed by dissociation to a Ni(IV) species, as has been observed for the oxidation of bis(dithiocarbamato) complexes of divalent nickel.[51] Work is in progress to establish the stoichiometry of the reaction and the identity of the reaction products.

Note Added in Proof. Since the submission of this paper, the preliminary results of a single crystal X-ray structure determination have become available (D. Taylor, personal communication). These confirm that the square-planar MS_4 coordination proposed above occurs in the compound $Ni(NH_2SacNH_2Sac)_2 \cdot 2DMF$.

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Registry No. NH_2SacNH_2SacH, 6944-34-9; $[Ni(NH_2SacNH_2SacH)_2]Cl_2$, 54062-04-3; $Ni(NH_2SacNH_2Sac)_2$, 41161-43-7; $Pd(NH_2SacNH_2Sac)_2$, 54003-31-5; $Pt(NH_2SacNH_2Sac)_2$, 54003-32-6; dithiobiuret, 541-53-7; bis(dithiobiureto)nickel(II), 24601-09-0; 3,5-diamino-1,2-dithiolium iodide, 5137-86-0; 3,5-dimethyl-1,2-dithiolium iodide, 22251-86-1; 3-methyl-5-phenyl-1,2-dithiolium iodide, 54003-51-9; 3,4,5-trimethyl-1,2-dithiolium iodide, 39703-73-6; 1,2-dithiolium iodide, 3163-68-6.

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