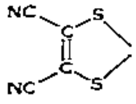
Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in the Netherlands.

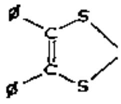
NEW STRUCTURES IN TRANSITION METAL CHEMISTRY

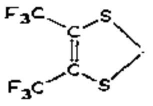
HARRY B. GRAY

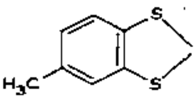
California Institute of Technology, Gates and Crellin Laboratories of Chemistry, Pasadena, Calif. (U.S.A.)

The independent reports in 1962 of the planar complexes[1a,1b] $Ni(mnt)_2^{2-}$ and $Ni(S_2C_2\Phi_2)_2$ have stimulated considerable interest in the coordination chemistry of this type of bidentate sulfur-donor ligand[2,3]. The ligands that have been most thoroughly investigated are shown below:

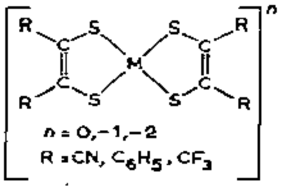

mnt


$S_2C_2\phi_2$

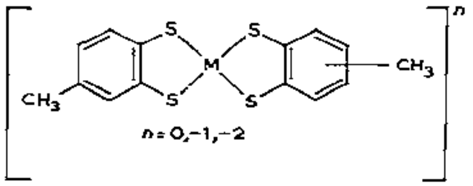

$S_2C_2(CF_3)_2$


tdt

With the late transition metals, these ligands form very stable planar complexes which are of particular interest because in most cases they exist in three states of oxidation with a given central metal. The general formulas I and II summarize this behavior:



(I)



(II)

M = Fe, Co, Rh, Ni, Pd, Pt, Cu, Ag, Au

The $n = -2$ complexes can be successfully formulated in the usual fashion as containing dianionic ligands and divalent metal ions. Two particularly interesting complexes in the $M(mnt)_2^{2-}$ series are $Rh(mnt)_2^{2-}$ and $Au(mnt)_2^{2-}$. Their prop-

TABLE I

STABLE, MONONUCLEAR Rh^{II} AND Au^{II} COMPLEXES

Complex	*Color*	μ_{eff}, *B.M.*	$\langle g \rangle$	$\langle a \rangle$
$[(n\text{-}C_4H_9)_4N]_2[Rh(mnt)_2]$	green	1.91	2.134	—
$[(n\text{-}C_4H_9)_4N]_2[Au(mnt)_2]$	green	1.89	2.009	41.9 (^{197}Au)

erties are given in Table I. These paramagnetic systems are considered to be the first well-authenticated examples of mononuclear Rh^{II} and Au^{II} complexes.

The series of tdt and mnt monoanionic complexes present a group of square planar complexes unique in their magnetic properties. The only monoanionic complexes that possess normal electronic structures are $Au(mnt)_2^-$ and $Au(tdt)_2^-$. These complexes are diamagnetic and can be reasonably formulated as containing Au^{III}. The interesting $Cu(tdt)_2^-$ and $Cu(mnt)_2^-$ complexes are diamagnetic and square planar. This represents a new spin state for copper in a stable square planar molecular matrix. The $M(tdt)_2^-$ complexes of Ni and Pt are spin-doublets and also represent unusual spin states for square planar complexes of these metals. The analogous mnt complexes with these metals[3] also have $S = 1/2$. The latter complexes undergo spin–spin exchange in the solids with the result that the observed magnetic moments are lower than expected at room temperature. This exchange interaction apparently is not effective in solid samples containing $Ni(tdt)_2^-$ and $Pt(tdt)_2^-$.

For all the above complexes, both di- and monoanionic, the even-electron systems are spin-singlets while the odd-electron systems are spin-doublets. The monoanionic complexes of iron and cobalt, however, do not fit into this pattern. A series of susceptibility measurements on analytically pure solid samples containing $Fe(tdt)_2^-$ and $Fe(mnt)_2^-$ indicate an $S = 1/2$ ground state for these compounds. However, solution susceptibility measurements in a wide range of solvents of varying polarity and coordinating power give moments that correspond to $S = 3/2$, a spin-quartet, for both complexes.

One possible explanation for the lower susceptibilities of the solids is exchange demagnetization. Weiher, *et al.*, in a recent magnetic-susceptibility study of solid samples containing $Ni(mnt)_2^-$, $Pd(mnt)_2^-$, and $Pt(mnt)_2^-$ proposed that the partially quenched paramagnetism observed in these complexes may be due to a pairwise interaction of the planar units leading to a singlet–triplet equilibrium[4]. The mechanism for this process was considered to involve spin–spin interactions of sulfur in the ligand system with pairs of metal ions. These workers suggested that $Fe(mnt)_2^-$ may also fit into the general scheme although they were unable to draw an analogous correlation with pairwise antiferromagnetic behavior. A second possibility is that the true ground state of isolated $Fe(mnt)_2^-$ and $Fe(tdt)_2^-$ units is a doublet, and that the higher moments in solution are the result of interaction of the anions with solvent. Consistent with this suggestion is the fact that the electronic spectrum of $Fe(tdt)_2^-$ is extensively perturbed by solvents. It is also possible that adsorbed or coordinated oxygen, particularly in the solid, may somehow affect magnetic measurements on complexes containing $Fe(mnt)_2^-$ and $Fe(tdt)_2^-$.

The most remarkable compound, however, of the entire series is $Co(tdt)_2^-$, which is a stable spin-triplet both in the solid and all solutions measured. In comparison, solid $Co(mnt)_2^-$ is diamagnetic. Thus $Co(tdt)_2^-$ represents the first example in chemistry of a well-authenticated square planar complex with a spin-triplet ground state.

In the system I and II complexes there are two limiting oxidation state formalisms. Considering the case where M = Ni, either the metal is formally oxidized (the classical oxidation-state formalism) or the ligand network (L_2) is formally oxidized, as follows:

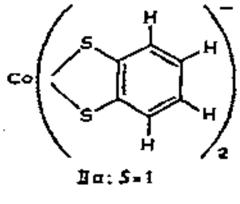
n:	*2−*	*1−*	*0*
metal oxidized	Ni^{II}	Ni^{III}	Ni^{IV}
ligands oxidized	L_2^{4-}	L_2^{3-}	L_2^{2-}

There is considerable evidence which indicates that the L_2^{3-} and L_2^{2-} formulations are preferable for the $n = -1$ and $n = 0$ complexes. Mention should be made of the strong ligand dependence of the polarographic half-wave potentials for the electron transfer reactions 2− → 1− and 1− → 0, and the unusual stability of the four-coordinate state in the $n = 1-$ and $n = 0$ complexes[2,3,14].

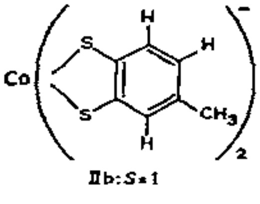
Molecular orbital calculations of $Ni(mnt)_2^{2-}$ and $Ni(mnt)_2^{-}$ indicate that the ordering of important energy levels is $xy(\sigma^*) > x^2-y^2(\pi^*) > xz(\pi^*)$, where the x axis bisects the two C═C lines[3]. The ground state electronic structure of $Ni(mnt)_2^{2-}$ is then $\ldots[xz(\pi^*)]^2[x^2-y^2(\pi^*)]^2$. The calculation of $Ni(mnt)_2^{-}$ indicates that both the $xz(\pi^*)$ and $x^2-y^2(\pi^*)$ levels are predominantly ligand based. This means that $Ni(mnt)_2^{-}$ approximately contains Ni^{II} and a mnt_2^{3-} ligand system. In other words, in our model the unpaired electron in $Ni(mnt)_2^{-}$ spends most of its time on the sulfur atoms, in a delocalized orbital network of x^2-y^2 symmetry.

The separation of $x^2-y^2(\pi^*)$ and $xz(\pi^*)$ is comparable to the value of electron-pairing energy in these complexes, as judged by the fact that $Co(mnt)_2^{-}$ is low spin (probable ground state $[xz(\pi^*)]^2$) and $Co(tdt)_2^{-}$ is high spin (probable ground state $[xz(\pi^*)]^1[x^2-y^2(\pi^*)]^1$. Since the $xz(\pi^*)$ level is conjugated with the $p\pi$ orbitals on the carbon atoms in systems I and II, electron-withdrawing substituents (R in system I and on the rings in system II) should stabilize $xz(\pi^*)$ relative to $x^2-y^2(\pi^*)$ and enhance the chances of obtaining low-spin systems. Strong electron-withdrawing groups may also lower the electron-pairing energy in the $xz(\pi^*)$ orbital by increasing the delocalization of this level.

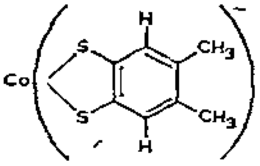
Thus, as a further test of our model, we have prepared[15] the six cobalt complexes IIa–IIf, with the results given below.



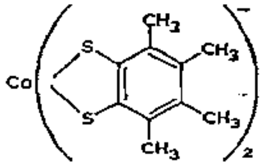
IIa: $S=1$



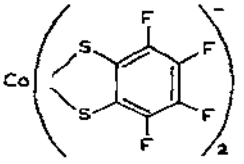
IIb: $S=1$



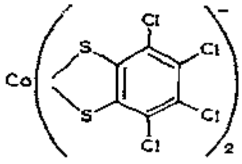
IIc: $S = 1$



IId: $S = 1$



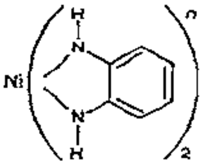
IIe: $S = 0$



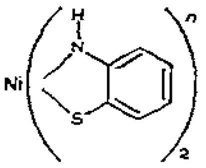
IIf: $S = 0$

The fact that there is a change from high spin to low spin as the electron-withdrawing groups Cl and F are introduced is consistent with our model in which the $S = 0$, $n = -1$ cobalt complexes are assigned the structure $[xz(\pi^*)]^2$.

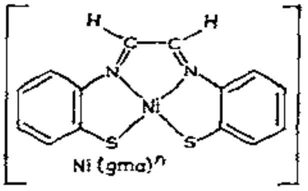
The classical oxidation-state formalism is shown to be inconsistent by examining the electronic structures of Ni complexes containing nitrogen as well as sulfur as a donor atom. The key systems are III, IV, and V, as shown below.



(III)



(IV)



(V)

The $n = 0$ III complex was originally claimed by Feigl and Fürth[5] but doubt has since been expressed concerning the number of hydrogens* attached to nitrogens. Our analytical and molecular weight results, including a mass spectrum with parent peak at $m/e = 270$, on a sample prepared by the published method agree with the original formulation III ($n = 0$). The $n = 0$ complex undergoes two reversible one-electron reductions to give the $n = -1$ and -2 complexes.

Complex IV($n = 0$) was prepared by a published method[7]. Analytical and molecular weight data, including a mass spectrum with parent peak at $m/e = 304$, establish formula IV($n = 0$) and are inconsistent with the original formulation[7] as a binuclear oxygen-bridged Ni^{IV} complex. Complex IV($n = 0$) shows two reversible reduction waves indicating the existence of the $n = -1$ and -2 complexes. Complex IV($n = -1$), prepared by BH_4^- reduction of IV($n = 0$), shows an e.s.r. spectrum with $\langle g \rangle = 2.055$ (DMF, DMSO, THF). The behavior of systems III

---

* Bardoděj prefers two less hydrogens on the nitrogens and formulates this as a nickel(II) species with oxidized ligands (*cf.* ref. 6).

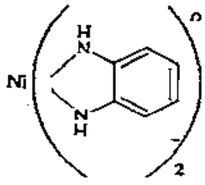
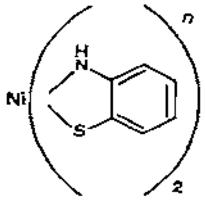
and IV suggests that the electron-transfer reactions common to the sulfur systems may be a more general phenomenon.

Complexes of Zn^{II} and Cd^{II} with glyoxal bis(2-mercaptoanil) (gma) have been prepared recently[8]. Using precisely the same synthetic procedure, we have prepared the Ni^{II} complex, Ni(gma) = V(n = 0). The Ni(gma) complex shows two polarographic reduction waves, indicating the existence of $Ni(gma)^-$ and $Ni(gma)^{2-}$.

The polarographic and e.s.r. data pertinent to this discussion are set out in Table II. The important point is the obvious electronic similarity of complexes

TABLE II

POLAROGRAPHIC AND ELECTRON SPIN RESONANCE RESULTS[a]

Complex	$E_{1/2}$[b]		*g values*[d] *for* $n = -1$			
	$n=0 \rightarrow n=-1$	$n=-1 \rightarrow n=-2$	$\langle g \rangle$	g_1	g_2	g_3
$Ni(tdt)_2{}^n$	c	−1.068	2.082	2.016	2.048	2.183
$Ni(mnt)_2{}^n$	c	− .218	2.063	1.996[e]	2.043[e]	2.140[e]
	−1.404	−2.075	2.034	c	c	c
	−0.720	−1.573	2.055	2.006	2.030	2.123
$Ni(gma)^n$	−0.823	−1.605	2.051	2.009	2.027	2.119

[a] Reproduced, with permission, from ref. 14.

[b] Potentials in volts measured in DMF using a dropping Hg electrode with a $Ag–AgClO_4$ reference electrode. Oscillopolarography was used to establish that all waves are due to reversible electron transfers.

[c] Accurate values are not available.

[d] $\langle g \rangle$ normally obtained in several solvents; g_1, g_2, and g_3 obtained from $DMF–CHCl_3$ glass at 77 °K unless otherwise noted.

[e] Glass at 100 °K.

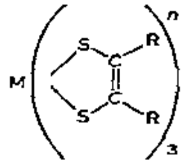
[f] Obtained in DMSO only.

IV(n = −1) and $Ni(gma)^-$. Their polarography, $\langle g \rangle$ values, and anisotropic g values are almost identical. The lack of axial symmetry in the g tensor rules out the d^9 Ni^I formulation for $Ni(gma)^-$, and the electronic similarity of IV(n = 1) with $Ni(gma)^-$ rules out the d^7, Ni^{III} formulation for IV(n = −1). The n = −1 complexes are both consistently formulated as Ni^{II}-radical–ligand complexes. In this scheme, the $n = 0$ complexes are assigned as Ni^{II}-radical–ligand complexes with both spin-singlet and spin-triplet ground states as possibilities in a molecular orbital system for the planar geometry. Thus the difference in the three possible members of each series I–V is then understood as a change in oxidation state of the ligand.

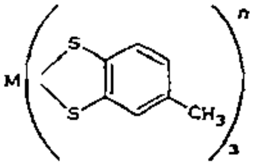
Examination of anisotropic g values for $Ni(mnt)_2^-$ and $Ni(tdt)_2^-$, obtained on oxidation of the classical Ni^{II} complexes $Ni(mnt)_2^{2-}$ and $Ni(tdt)_2^{2-}$, reveals that these complexes are electronically similar to IV($n = -1$) and $Ni(gma)^-$. Thus again the Ni^{II}-radical–ligand formulation is applicable.

As final examples illustrating the change in oxidation state of the ligand, Zn(gma) and Cd(gma) can be reduced to stable mono-anions using chemical reducing agents such as BH_4^-. The resulting $Zn(gma)^-$ and $Cd(gma)^-$ complexes have $S = 1/2$ and show e.s.r. spectra in solution with $g = 2.006$ (Zn) and $g = 2.004$ (Cd). These complexes are among the first examples of Zn and Cd complexes with one unpaired electron.

With the early transition metals, the ligands form six-coordinate complexes of the two basic types (VI) and (VII):



(VI)



(VII)

$R = CF_3, C_6H_5$
$n = 0, -1, -2$
$R = CN$
$n = -2, -3$
M = V, Cr, Mo, W, Re, Fe, Ru, Os, Co

$n = 0, -1, -2$

Notice that the classical oxidation-state formalism is inadequate for these systems since, for example, $V(S_2C_2\Phi_2)_3$ would call for V^{VI}. Again we formulate the complexes as M-radical-ligand systems.

The six-coordinate complexes are of unusual interest due to the fact that the $Re(S_2C_2\Phi_2)_3$ complex has been shown to have, instead of the usual octahedral structure, a near-perfect trigonal-prismatic array of donor atoms in a crystalline sample[10]. A perspective drawing of the basic structure is shown in Fig. 1.

We now consider the possibility that some or all of the (VI) and (VII) complexes are also trigonal prismatic. It is helpful at this point to outline some important physical properties of $Re(S_2C_2\Phi_2)_3$. Green crystals of $Re(S_2C_2\Phi_2)_3$ are soluble in most organic solvents. The solid sample has a magnetic moment of 1.79 *B.M.* and in $CHCl_3$ or THF gives a single broad e.s.r. line (width ~ 75 gauss) at $g = 2.015 \pm 0.003$. Furthermore, a polycrystalline sample shows only one broad line (width ~60 gauss), also at $g = 2.015 \pm 0.003$. This line appears to be sym-

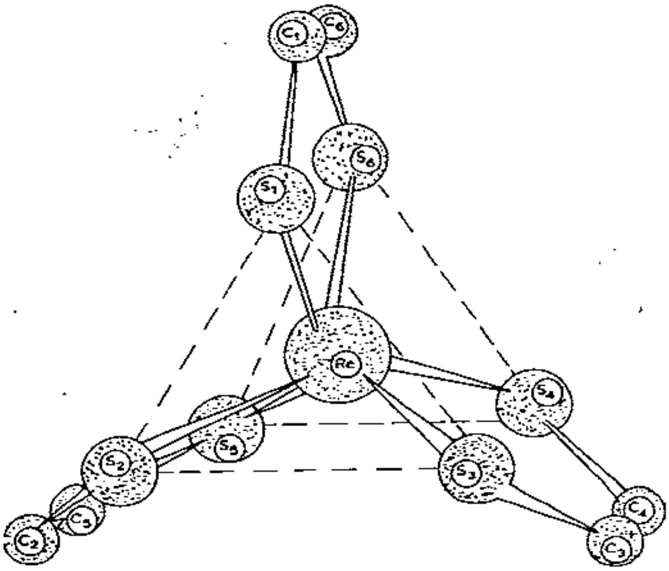


Fig. 1. Structure of $Re(S_2C_2\Phi_2)_3$. The Φ groups have been omitted for simplicity. [Reproduced, with permission, from ref. 10].

metrical, indicating little if any anisotropy in the g tensor. The striking similarity of these e.s.r. spectra of $Re(S_2C_2\Phi_2)_3$ indicates that there is no significant change in the ReS_6 structure in going from solid to solution. In further support, the lowest band maxima in the solution absorption spectrum of $Re(S_2C_2\Phi_2)_3$ in $CHCl_3$ occur at 8230 cm^{-1} ($\varepsilon = 1090$), 14,050 cm^{-1} ($\varepsilon = 24{,}000$), and 23,450 cm^{-1} ($\varepsilon = 12{,}300$). In a solid sample, the lowest maxima are at 8000, 13,500, and 23,000 cm^{-1} ($\pm$ 200 cm^{-1}). Thus we conclude that $Re(S_2C_2\Phi_2)_3$ also has a trigonal-prismatic structure in solution.

The e.s.r. spectrum of $Re(S_2C_2\Phi_2)_3$ in a DMF–$CHCl_3$ glass (77 °K) consists of many hyperfine lines and it is apparent that there is little if any anisotropy in the g tensor, since all patterns are centered at the same g value of 2.015 ± 0.003. We shall use the results of this experiment to establish trigonal-prismatic structures in the series.

$M(tdt)_3^n$ (series VII). Direct comparison with $Re(S_2C_2\Phi_2)_3$ is obtained with $Re(tdt)_3$.

The green $Re(tdt)_3$ complex shows a single broad e.s.r. line (width ~100 gauss) at $g = 2.010 \pm 0.003$ in $CHCl_3$ or THF and a similar single line in a polycrystalline solid at $g = 2.010 \pm 0.003$ (width ~70 gauss). The band maxima in the $CHCl_3$ solution absorption spectrum of $Re(tdt)_3$ are quite similar to those of $Re(S_2C_2\Phi_2)_3$. In addition, $Re(tdt)_3$ shows precisely the pattern of $Re(S_2C_2\Phi_2)_3$ in its e.s.r. spectrum at 77 °K in a DMF–$CHCl_3$ glass (although the hyperfine interactions are slightly larger). We conclude that Re(tdt)$_3$ also has a trigonal-prismatic array of donor atoms.

We can now compare the magnetic properties of Re($S_2C_2\Phi_2$)$_3$ and Re(tdt)$_3$ with those of the electronically similar complexes[11-13] ML_3^- [M = Cr, Mo, W; L = tdt, $S_2C_2\Phi_2$, $S_2C_2(CF_3)_2$] and VL_3^{2-} (L = tdt, bdt, $S_2C_2\Phi_2$, mnt)[15]. In the ML_3^- and VL_3^{2-} complexes the *g* tensor has been found to be nearly isotropic. In addition, the magnetic moments of Re($S_2C_2\Phi_2$)$_3$ and Φ_4As[W($S_2C_2\Phi_2$)$_3$] are almost identical (1.79 *vs.* 1.77 *B.M.*). Although more data bearing on structure are needed, it is probable from the above results that all the ML_3^- and VL_3^{2-} complexes possess a stable state with the unusual trigonal-prismatic geometry.

We gratefully acknowledge the support of the National Science Foundation and Public Health Service Research Grant CA–07016–03 from the National Cancer Institute.

REFERENCES

1 H. B. Gray, R. Williams, I. Bernal and E. Billig, *J. Am. Chem. Soc.*, 84 (1962) 3596; (b) G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, 84 (1962) 3221.

2 S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams and H. B. Gray, *J. Am. Chem. Soc.*, 86 (1964) 4594; and references contained therein.

3 H. B. Gray, *This Volume*, p. 239.

4 J. F. Weiher, L. R. Melby and R. E. Benson, *J. Am. Chem. Soc.*, 86 (1964) 4329.

5 F. Feigl and M. Fürth, *Monatsh.*, 48 (1927) 445.

6 Z. Bardoděj, *Collection Czech. Chem. Comm.*, 20 (1955) 176.

7 W. Hieber and R. Brück, *Z. Anorg. Chem.*, 269 (1952) 13.

8 H. Jadamus, Q. Fernando and H. Freiser, *J. Am. Chem. Soc.*, 86 (1964) 3056.

9 E. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, 87 (1965) 4012; and references therein.

10 R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, 87 (1965) 3776.

11 J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer and H. W. Finck, *J. Am. Chem. Soc.*, 86 (1964) 4198.

12 A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *J. Am. Chem. Soc.*, 86 (1964) 2799.

13 A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *Inorg. Chem.*, 4 (1965) 55.

14 E. Stiefel, J. H. Waters, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 87 (1965) 3016.

15 M. J. Baker and H. B. Gray, to be published.