The Toluenedithiolate and Maleonitriledithiolate Square-Matrix Systems

Raymond Williams, E. Billig, James H. Waters, and Harry B. Gray

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received June 29, 1965*

Abstract: The syntheses and properties of bis(toluene-3,4-dithiolate) square-planar complexes of Cu, Au, Ni, Pt, Co, and Fe are reported. Polarographic results confirm that the complexes are best described using a molecular orbital formulation of the bonding in which the sulfur-donor ligand assumes a commanding role. The magnetic ground states of the $M(tdt)_2^-$ complexes are among the first examples of their electronic structural type for a square-planar situation. With M = Ni and Pt, stable spin-doublet complexes are obtained. With M = Co, a stable spin-triplet complex is obtained. The spectral and magnetic properties of the $M(tdt)_2^{n-}$ complexes are discussed and compared with properties of the related bis(maleonitriledithiolate) planar complexes. Stable complexes of formulas $R_2[M(tdt)]_2$ and $R[M(tdt)_2]$ have been characterized with M = Cu, Ni, and Pt. Polarographic evidence indicates the existence of complexes of both formulas with M = Co, Fe, and Au, although only the unusual $R[M(tdt)_2]$ complexes have been characterized in these cases.

Numerous papers and communications recently have been published concerning the characterization and electronic structures of square-planar metal complexes containing sulfur-donor ligands.[1] In particular, the complexes of four such ligands have received considerable attention. These ligands, in dianionic form, are maleonitriledithiolate (mnt^{2-}), toluene-3,4-dithiolate (tdt^{2-}), *cis*-stilbenedithiolate [$(C_6H_5)_2C_2S_2^{2-}$], and *cis*-1,2-bis(trifluoromethyl)ethylenedithiolate [$(CF_3)_2C_2S_2^{2-}$]. Among the new or unusual electronic structural types for a planar situation produced in the course of this work have been complexes of copper with $S = 0$, paramagnetic complexes of nickel, palladium, and platinum with $S = {}^1/_2$, complexes of cobalt with $S = 0$ and $S = 1$, a paramagnetic complex of rhodium with $S = {}^1/_2$, and paramagnetic complexes of iron with $S = {}^3/_2$ and possibly $S = {}^1/_2$. The present work describes in detail the preparation and characterization of the bis-tdt complexes of copper, gold, nickel, platinum, cobalt, and iron. Polarographic, magnetic susceptibility, e.s.r., and optical spectral results are presented. Comparisons are made with the properties of analogous mnt complexes, including the paramagnetic $Ag(mnt)_2^{2-}$ and $Au(mnt)_2^{2-}$ complexes.

A general discussion of the electronic structures of the new planar complexes of tdt and mnt is presented. Emphasis is placed on the cobalt complexes which have spin-singlet and spin-triplet ground states.

Experimental Section

Chemicals. Toluene-3,4-dithiol was obtained from Eastman Organic Chemicals and was used without further purification. All other chemicals were of reagent grade and were used without further purification.

Preparation of Compounds. $[(n\text{-}C_4H_9)_4N][Co(tdt)_2]$. Potassium metal (1.20 g., 0.030 g.-atom) was dissolved in 25 ml. of absolute ethanol. Toluene-3,4-dithiol (2.16 g., 0.014 mole) was added, followed by $CoCl_2 \cdot 6H_2O$ (1.60 g., 0.007 mole) in 10 ml. of absolute ethanol. An intense blue-green color appeared, which soon turned dark blue. A solution of $(n\text{-}C_4H_9)_4NBr$ (2.40 g., 0.0074 mole) in 20 ml. of absolute ethanol was added. The mixture was cooled in ice and filtered, and the precipitate was washed with 2-propanol and ether and air dried. The solid was dissolved in 50 ml. of warm acetone and filtered. The filtrate was concentrated to 5 ml. under reduced pressure and 2-propanol was added to precipitate the complex. The mixture was cooled, filtered, washed, and dried as before. The crude material (3.60 g.) was recrystallized twice from 3:1 v./v. ethanol–acetone and dried at 80° *in vacuo* to give 2.20 g. of dark blue plates.

$[(n\text{-}C_4H_9)_4N][Ni(tdt)_2]$. To a solution of potassium metal (1.25 g., 0.032 g.-atom) in 30 ml. of absolute ethanol was added 2.46 g. (0.016 mole) of toluene-3,4-dithiol. A solution of $NiCl_2 \cdot 6H_2O$ (1.84 g., 0.0077 mole) in 20 ml. of absolute ethanol was added, whereupon an intense red-brown color appears. $(n\text{-}C_4H_9)_4NBr$ (5.06 g., 0.0157 mole) in 15 ml. of absolute ethanol was added to the mixture, which was then allowed to stand for 1 hr. with occasional agitation. The mixture was filtered and the green precipitate obtained was treated in the same manner as the Co compound to give 2.47 g. $[(n\text{-}C_4H_9)_4N][Ni(tdt)_2]$ as green-black needles.

$[(n\text{-}C_4H_9)_4N][Cu(tdt)_2]$. To a solution of potassium metal (1.073 g., 0.028 g.-atom) in 30 ml. of absolute ethanol was added 2.798 g. (0.0179 mole) of toluene-3,4-dithiol, followed by 1.52 g. (0.009 mole) of $CuCl_2 \cdot 2H_2O$ in 15 ml. of absolute ethanol. An intense red-brown color appeared immediately. A solution of 4.00 g. (0.0125 mole) of $(n\text{-}C_4H_9)_4NBr$ in 15 ml. of absolute ethanol was added. After standing 6 hr. with occasional stirring, the mixture was green throughout. It was cooled and filtered, and the precipitate was treated in the same manner as the Co compound to give 4.41 g. of $[(n\text{-}C_4H_9)_4N][Cu(tdt)_2]$ as lustrous dark green plates.

$[(n\text{-}C_4H_9)_4N][Au(tdt)_2]$. To a solution of potassium metal (1.101 g., 0.0282 g.-atom) in 30 ml. of absolute ethanol was added 2.392 g. (0.0153 mole) of toluene-3,4-dithiol, followed by a solution of 2.46 g. (0.0076 mole) of powdered $(n\text{-}C_4H_9)_4NBr$ in 10 ml. of absolute ethanol. A solution of 4.8 g. (0.008 mole) of $KAuBr_4 \cdot 2H_2O$ in 30 ml. of absolute ethanol was added. A heavy green precipitate formed. The mixture was cooled in ice and filtered. The precipitate was washed with 2-propanol and ether and then air dried. The crude complex was recrystallized three times from methylene chloride–ethanol, yielding 3.28 g. of $[(n\text{-}C_4H_9)_4N][Au(tdt)_2]$ as green plates.

$[(n\text{-}C_4H_9)_4N][Pt(tdt)_2]$. Toluene-3,4-dithiol (2.387 g., 0.015 mole) was added to 30 ml. of N,N-dimethylformamide. Absolute ethanol (20 ml.) containing 3.43 g. (0.0066 mole) of $H_2PtCl_6 \cdot 6H_2O$ was slowly added. The solution turned light green, then purple, and finally black. The flask was warmed, and 0.900 g. of $NaBH_4$ (0.0238 mole) was added in small portions with vigorous shaking after each addition. The solution became purple, then green, then brownish green. $(n\text{-}C_4H_9)_4NBr$ (2.14 g., 0.0066 mole) was added and the solvent removed under reduced pressure. The residue was dissolved in methylene chloride and filtered, and the filtrate was concentrated under reduced pressure. Warm ethanol containing a little $(n\text{-}C_4H_9)_4NOH$ was added, and the solution was set aside to cool. The resulting precipitate was filtered and washed with absolute ethanol and ether. The crude complex was recrystal-

---

(1) See, for example: (a) H. B. Gray, *Progr. Transition Metal Chem.*, 1, 239 (1965); (b) A. L. Balch, F. Rohrscheid, and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965); (c) A. Davison and D. V. Howe, *Chem. Commun.* (London), 290 (1965); (d) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965); (e) E. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965); (f) J. H. Waters and H. B. Gray, *ibid.*, **87**, 3534 (1965).

Table I. Analytical Data for $R[M(tdt)_2]$ and $R_2[M(tdt)_2]$ Complexes

	% C		% H		% N		% S	
Complex	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(n\text{-}C_4H_9)_4N][Fe(tdt)_2]$	59.38	59.23	7.97	7.84	2.31	2.24	21.14	21.07
$[(n\text{-}C_4H_9)_4N][Co(tdt)_2]$	59.08	59.30	7.93	8.03	2.30	2.39	21.03	21.23
$[(n\text{-}C_4H_9)_4N][Ni(tdt)_2]$	59.10	59.48	7.94	7.85	2.30	2.23	21.04	21.21
$[(n\text{-}C_4H_9)_4N][Cu(tdt)_2]$	58.63	58.51	7.87	7.76	2.28	2.15	20.88	20.65
$[(n\text{-}C_4H_9)_4N][Au(tdt)_2]$	48.17	47.98	6.47	6.35	1.87	1.87	17.15	17.31
$[(n\text{-}C_4H_9)_4N][Pt(tdt)_2]$	48.29	47.33	6.48	6.25	1.88	1.76	17.19	16.80
$[(n\text{-}C_4H_9)_4N][Fe(tdt)_2\cdot C_5H_5N]$	61.28	61.38	7.79	7.93	4.08	3.94	18.70	18.97
$[(C_6H_5)_3As(CH_3)]_2\text{-}[Cu(tdt)_2]$	61.56	61.52	4.77	4.79	...	...	...	...
$[(C_6H_5)_3As(CH_3)]_2\text{-}[Ni(tdt)_2]$	61.85	61.37	4.79	4.78	...	...	...	...
$[(C_6H_5)_4As]_2[Pt(tdt)_2]$	58.62	57.02	4.13	4.17	...	...	10.09	10.12
$[(C_6H_5)_3As(CH_3)]\text{-}[Cu(tdt)_2]$	57.17	57.40	4.36	4.82	...	...	...	...

lized twice from ethanol–pyridine, yielding 2.8 g. of $[(n\text{-}C_4H_9)_4N][Pt(tdt)_2]$, as green needles. The product was dried at 80° *in vacuo.*

$[(C_6H_5)_4As]_2[Pt(tdt)_2]$. A solution of 0.78 g. (0.005 mole) of toluene-3,4-dithiol and 0.40 g. (0.01 mole) of NaOH in 20 ml. of water was degassed by freezing in Dry Ice, evacuating, thawing, and repeating this cycle several times. A similarly degassed solution of K_2PtCl_4 (0.52 g., 0.00125 mole) in 10 ml. of water was added under a rapid stream of nitrogen. In the same way, a degassed solution of 1.20 g. (0.00287 mole) of $(C_6H_5)_4AsCl$ in 10 ml. of water was added. The mixture was filtered in a drybox under nitrogen. The crude orange product was washed several times under nitrogen with acetone. The product was dried *in vacuo* with exclusion of light. It was not recrystallized.

$[(n\text{-}C_4H_9)_4N][Fe(tdt)_2]$ and $[(n\text{-}C_4H_9)_4N][Fe(tdt)_2\cdot C_5H_5N]$. To a solution of potassium metal (1.123 g., 0.0287 g.-atom) in 30 ml. of absolute ethanol was added 2.757 g. (0.0176 mole) of toluene-3,4-dithiol, followed by 1.458 g. (0.009 mole) of $FeCl_3$ in 20 ml. of hot ethanol. A very intense purple-red color appeared immediately. A solution of 3.90 g. (0.0121 mole) of $(n\text{-}C_4H_9)_4NBr$ in 20 ml. of absolute ethanol was added. The mixture was allowed to stand 0.5 hr., then was cooled in ice, and filtered. The precipitate was washed with ethanol and ether and dried. The precipitate was dissolved in 20 ml. of pyridine, and the solution was filtered. 2-Propanol (100 ml.) was added to the filtrate, which was cooled in an ice bath. The precipitate which formed was filtered, washed with 2-propanol, and dried at 0° *in vacuo.* Repetition of the recrystallization gave 3.30 g. of $[(n\text{-}C_4H_9)_4N][Fe(tdt)_2\cdot C_5H_5N]$, appearing as small, irregularly shaped red plates under the microscope. A portion of this compound was heated for 4 hr. at 80° *in vacuo* to remove the pyridine. $[(n\text{-}C_4H_9)_4][Fe(tdt)_2]$ was obtained, appearing as small irregular purple crystals under the microscope.

$[(C_6H_5)_3As(CH_3)]_2[Cu(tdt)_2]$. Sodium metal (0.750 g., 0.033 g.-atom) was dissolved in 30 ml. of absolute ethanol, and toluene-3,4-dithiol (2.133 g., 0.0136 mole) and $(C_6H_5)As(CH_3)I$ (5.6 g., 0.0125 mole) were added. $CuCl_2\cdot 2H_2O$ (1.165 g., 0.0068 mole) was dissolved in 30 ml. of tetrahydrofuran. All solvents were carefully degassed prior to use, and subsequent operations were carried out under nitrogen. The solution containing the metal salt was slowly added to the warm tdt solution and allowed to stand for 90 min. A red-brown precipitate formed. The mixture was cooled in ice and filtered, and the precipitate was washed with 3:1 (v./v.) tetrahydrofuran–ethanol, and finally with ether. The dry solid was recrystallized from 60 ml. of a solvent consisting of 6:6:1 (v./v./v.) tetrahydrofuran–methanol–dimethylformamide, washed with 1:1 (v./v.) tetrahydrofuran–ether and ether, and dried *in vacuo* to give 1.6 g. of orange-brown plates. The compound was stored under nitrogen.

The light red $[(C_6H_5)As(CH_3)]_2[Ni(tdt)_2]$ was prepared in the same manner.

Physical Measurements. Electronic spectra were measured using a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used throughout. Infrared spectra were measured with a Perkin-Elmer Model 441 spectrophotometer using the KBr wafer technique. Static susceptibility measurements were made at room temperature by the Gouy method using $Hg[Co(SCN)_4]$,[2] nickel chloride solution,[2] and $Cs_2[CoCl_4]$ solution[3] as calibrants for solid and solution moments. Conductances were determined on an Industrial Instruments Bridge, Model RC16B2, using a cell calibrated with 0.02 *M* KCl solution. Polarographic measurements were made in DMF solution with a dropping mercury electrode in a three-electrode cell, using an electronic polarograph described elsewhere.[4] Triangular wave chronoamperometry (oscillopolarography) was utilized, with a platinum electrode serving as indicator electrode. Silver–silver perchlorate was used as the reference electrode ($Ag/AgClO_4$, 0.1 *M;* $[(C_3H_7)_4N][ClO_4]$, 0.1 *M*). Solutions were approximately 10^{-3} *M* in complex and 10^{-1} *M* in tetra-*n*-propylammonium perchlorate. Electron spin resonance spectra were recorded by using a Varian V-4502 spectrometer with 100-kc. field modulation, operating at 9500 Mc. A Norelco X-ray machine, with Cu Kα radiation and a nickel filter, was used for measuring X-ray powder patterns.

Results

Analytical data that establish the formulas $R_2[M(tdt)_2]$ and $R[M(tdt)_2]$ are given in Table I. Conductances, melting points, and magnetic moments are given in Table II. In nitromethane[5] and in dimethylformamide the $R[M(tdt)_2]$ complexes appear to be 1:1 electrolytes. The most prominent infrared bands are given in Table III. Table IV gives X-ray powder diffraction data for the $[(C_6H_5)_3As(CH_3)][M(tdt)_2]$ complexes with M = Ni, Pt, Co, Cu, and Au. The compounds appear to be isomorphous and are assumed to be square-planar by analogy to the related systems $[(n\text{-}C_4H_9)_4N][M(mnt)_2]$.[6]

Polarographic Results. A summary of polarographic potentials for bis complexes of tdt and of related sulfur-donor ligands is given in Table V. The stability of the monoanion relative to the dianion is greater for the tdt complexes than for the corresponding complexes of mnt.

The most significant result that emerges from consideration of these potentials is their tremendous variation, as the ligand is changed, for complexes of the same metal and charge type. For every metal investigated so far, the difference between the potentials for the mnt complexes and that for the tdt complexes is in the vicinity of 1 v. By contrast, the potentials for the

---

(2) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 406.

(3) B. N. Figgis, *J. Chem. Soc.*, 3423 (1964).

(4) M. J. Kelley, J. D. Fisher, and K. C. Jones, *Anal. Chem.*, 31, 1475 (1959); 32, 1262 (1960).

(5) Conductance ranges in nitromethane have been given by N. S. Gill and R. H. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(6) J. D. Forrester, A. Zalkin, and D. Templeton, *Inorg. Chem.*, 3, 1507 (1964).

Table II. Physical Properties of $R[M(tdt)_2]$ and $R_2[M(tdt)_2]$ Complexes

Complex	M.p., °C.	Λ^a	μ_{eff} (solid), B.M.	μ_{eff} (soln.), B.M.
$[(n\text{-}C_4H_9)_4N]][Fe(tdt)_2]$	232–234	65	2.07	3.87^b $3.77^{c,d}$
$[(n\text{-}C_4H_9)_4N][Co(tdt)_2]$	152–153	75	3.18	3.37^e 3.43^b 3.33^d
$[(n\text{-}C_4H_9)_4N][Ni(tdt)_2]$	152–153	65	1.79	2.20^d
$[(n\text{-}C_4H_9)_4N][Cu(tdt)_2]$	152–153	68	Diamagnetic	Diamagnetic[d]
$[(n\text{-}C_4H_9)_4N][Au(tdt)_2]$	152–153	69	Diamagnetic	Diamagnetic[d]
$[(n\text{-}C_4H_9)_4N][Pt(tdt)_2]$	160–161	67	1.77	2.01^d
$[(n\text{-}C_4H_9)_4N][Fe(tdt)_2 \cdot C_5H_5N]$	232–234[f]	68	3.84	g
$[(C_6H_5)_3As(CH_3)]_2[Cu(tdt)_2]$	92–95 dec.	120^d	1.78	g
$[(C_6H_5)_3As(CH_3)]_2[Ni(tdt)_2]$	131–134	110^d	Diamagnetic	g
$[(C_6H_5)_3As(CH_3)][Cu(tdt)_2]$	146–148	57^d	g	g

[a] Measured at *ca.* 25°, in nitromethane, unless otherwise indicated. [b] DMSO solution. [c] For $[(C_6H_5)_4As][Fe(tdt)_2]$. [d] DMF solution. [e] Acetone solution. [f] Gives off pyridine, 130–170°. [g] Not measured.

Table III. Infrared Spectra of Some $[(n\text{-}C_4H_9)_4N][M(tdt)_2]$ Complexes

Complex	Infrared band maxima, cm.$^{-1}$
$[(n\text{-}C_4H_9)_4N][Fe(tdt)_2]$	3020, 2940, 2860, 1465, 1440, 1370, 1270, 1235, 1195, 1165, 1135, 1120, 1095, 1015, 855, 790, 730, 680
$[(n\text{-}C_4H_9)_4N][Fe(tdt)_2 \cdot C_5H_5N]$	3015, 2940, 2860, 1830, 1560, 1520, 1460, 1440, 1365, 1265, 1230, 1200, 1130, 1120, 1090, 1060, 1020, 855, 785, 740, 725, 680
$[(n\text{-}C_4H_9)_4N][Co(tdt)_2]$	3015, 2935, 2865, 1565, 1520, 1465, 1440, 1365, 1270, 1240, 1200, 1165, 1140, 1125, 1095, 1015, 870, 805, 730, 680
$[(n\text{-}C_4H_9)_4N][Ni(tdt)_2]$	3010, 2935, 2860, 1565, 1520, 1465, 1440, 1365, 1280, 1235, 1195, 1165, 1140, 1080, 1015, 865, 800, 730, 680
$[(n\text{-}C_4H_9)_4N][Cu(tdt)_2]$	3020, 2940, 2860, 1525, 1465, 1440, 1370, 1270, 1240, 1200, 1165, 1135, 1125, 1100, 1015, 870, 855, 795, 730, 680
$[(n\text{-}C_4H_9)_4N][Pt(tdt)_2]$	3005, 2940, 2850, 1565, 1505, 1460, 1430, 1365, 1280, 1230, 1190, 1160, 1135, 1095, 1065, 1015, 865, 790, 730, 680
$[(n\text{-}C_4H_9)_4N][Au(tdt)_2]$	3015, 2940, 2855, 1520, 1460, 1440, 1365, 1260, 1235, 1195, 1130, 1100, 1010, 860, 790, 730, 680
Toluene-3,4-dithiol	3035, 3010, 2940, 2910, 2855, 2725, 2525, 1880, 1725, 1600, 1570, 1530, 1430, 1370, 1260, 1210, 1115, 1025, 915, 855, 785, 730, 680

Table IV. X-Ray Diffraction Results for Some $[(C_6H_5)_3As(CH_3)][M(tdt)_2]$ Complexes

Complex	Interplanar spacings (Å.) of the most prominent peaks
$[(C_6H_5)_3As(CH_3)][Co(tdt)_2]$	9.31(vs), 8.67(m), 7.50(s), 7.13(w), 6.82(w), 6.37(w), 5.91(w), 5.50(w), 5.28(w), 5.04(w), 4.82(w), 4.72(vs), 4.62(m), 4.53(m), 4.39(m), 4.35(m), 4.17(s), 3.90(w), 3.78(m)
$[(C_6H_6)_3As(CH_3)][Ni(tdt)_2]$	9.31(vs), 8.59(m), 7.70(s), 7.13(w), 6.82(w), 5.87(m), 5.30(w), 5.04(w), 4.75(s), 4.70(s), 4.53 (w), 4.29(w), 4.15(s), 3.83(w)
$[(C_6H_5)_3As(CH_3)][Cu(tdt)_2]$	9.31(vs), 8.67(m), 7.57(s), 7.20(w), 6.76(w), 6.15(w), 5.87(w), 5.28(w), 5.05(w), 4.72(s), 4.62 (m), 4.53(w), 4.42(w), 4.27(w), 4.17(vs), 3.85(w), 3.75(w)
$[(C_6H_5)_3As(CH_3)][Pt(tdt)_2]$	9.50(vs), 8.67(m), 7.63(s), 7.20(w), 6.76(m), 6.20(m), 5.87(m), 5.43(w), 5.30(w), 4.75(s), 4.65 (w), 4.35(w), 4.19(vs), 3.86(w), 3.75(w)
$[(C_6H_5)_3As(CH_3)][Au(tdt)_2]$	9.41(vs), 8.67(m), 7.76(s), 7.31(w), 6.82(w), 6.23(w), 5.80(m), 5.37 (w), 5.15(m), 4.87(w), 4.70(vs), 4.60(w), 4.50(m), 4.33(w), 4.17 (m), 4.09(m), 3.88(w)

monoanionic bis complexes of any one ligand with the entire series of metals cover a much smaller range. The conclusion appears inescapable that the ligand is assuming a commanding role in the ease of reduction and must participate somehow in the electron-transfer process. This conclusion supports our contention[1e,7,8] that, in the monoanionic and neutral complexes, the ligand has radical-anion character to an extent that varies with the electron-rich or electron-poor nature of the ligand. It seems clear that classical oxidation-state formalism cannot adequately describe these complexes. Therefore, we present, in a later section, what we believe to be a truer picture of the electronic structure of these complexes in terms of molecular orbital theory.

The polarographic results indicate the existence of several reduced species, some of which have been obtained by chemical reduction. Solutions which

---

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

(8) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *ibid.*, **86**, 2598 (1964).

Table V. Polarographic Half-Wave Potentials for the Reaction[a] $ML_2^{2-} \rightleftarrows ML_2^- + e^-$

L	M						
	Cu	Ni	Pd	Pt	Co	Fe	Au
tdt	−1.15	−1.07		−1.05	−1.41	−1.46	−1.95
$(C_6H_5)_2C_2S_2$		−1.309			−1.420		
		−0.74[c]					
$(CF_3)_2C_2S_2$		−0.121[b]	+0.081[b]	−0.267[b]	−0.398[b]		
mnt	−0.201	−0.218	−0.001	−0.231	−0.384	−0.862	−0.961
	0.330[b]	0.226[b]	0.440[b]	0.210[b]	0.050[b]		

[a] Measured in DMF solution relative to $Ag/AgClO_4$ reference electrode unless otherwise indicated. Potentials in volts. [b] In acetonitrile, relative to calomel electrode: A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964). [c] In DMSO, relative to calomel electrode: Davison, *et al.*, footnote *b*.

probably contain $Fe(mnt)_2^{2-}$ and $Co(tdt)_2^{2-}$ have been obtained by chemical reduction of the corresponding monoanions. Similarly, $Au(mnt)_2^{2-}$ has been obtained in DMF–diglyme solution at low temperature and has been identified by its e.s.r. spectrum. The stable, green $[(n\text{-}C_4H_9)_4N]_2[Au(mnt)_2]$ complex has been isolated and characterized.[1f] The reduction potential of $Au(tdt)_2^-$ is much higher than that of $Au(mnt)_2^-$, and its chemical reduction to $Au(tdt)_2^{2-}$ has not been accomplished.

Magnetic Properties. A summary of the spin ground states for planar tdt complexes and, for comparison, those of planar mnt complexes is presented in Table VI.

Table VI. Ground-State Spins of Planar Metal tdt and mnt Complexes

tdt complexes	S values	mnt complexes	S values
$Cu(tdt)_2^{2-}$	$^1/_2$	$Cu(mnt)_2^{2-}$	$^1/_2$
$Cu(tdt)_2^-$	0	$Cu(mnt)_2^-$	0
$Au(tdt)_2^-$	0	$Au(mnt)_2^{2-}$	$^1/_2$
$Ni(tdt)_2^{2-}$	0	$Au(mnt)_2^-$	0
$Ni(tdt)_2^-$	$^1/_2$	$Ni(mnt)_2^{2-}$	0
$Pt(tdt)_2^{2-}$	0	$Ni(mnt)_2^-$	$^1/_2$
$Pt(tdt)_2^-$	$^1/_2$	$Pd(mnt)_2^{2-}$	0
$Co(tdt)_2^-$	1	$Pd(mnt)_2^-$	$^1/_2$
$Fe(tdt)_2^-$	$(^1/_2)?, ^3/_2$	$Pt(mnt)_2^{2-}$	0
		$Pt(mnt)_2^-$	$^1/_2$
		$Co(mnt)_2^{2-}$	$^1/_2, (^3/_2)?$
		$Co(mnt)_2^-$	0, (1)
		$Rh(mnt)_2^{2-}$	$^1/_2$
		$Fe(mnt)_2^-$	$(^1/_2)?, ^3/_2$

Dianionic Complexes. The dianionic complexes of Ni, Pd, and Pt of both tdt and mnt are diamagnetic ($S = 0$), the normal spin states associated with these metal ions in a square-planar environment. Similarly, both $Cu(tdt)_2^{2-}$ and $Cu(mnt)_2^{2-}$ are spin doublets and may thus be regarded as classical Cu(II) complexes. Measurements of electronic spectra of all the dianionic mnt complexes under different conditions of potential ligand perturbation, coupled with e.s.r. studies of $Cu(mnt)_2^{2-}$ in different solvents, have firmly established that there is no appreciable ligand coordination of any kind in axial positions.[9] However, there is evidence for ligand coordination in axial positions in certain of the monoanionic complexes, as will be discussed later.

Paramagnetic, planar Ag(II) is still rare. We have e.s.r. evidence for the existence of $Ag(mnt)_2^{2-}$ (see Table IX), but to date we have not obtained salts of $Ag(mnt)_2^{2-}$ completely free of impurities. The $Au(mnt)_2^{2-}$ complex with $S = {}^1/_2$ is an authentic example of Au(II) in a planar situation. Attempts to prepare $Au(tdt)_2^{2-}$ have failed, as was noted above. The chemistry of silver with tdt^{2-} has not yet been explored in our laboratories, but in analogy with mnt^{2-}, there is reason to predict the complexes $Ag(tdt)_2^-$ and $Ag(tdt)_2^{2-}$.

The magnetic ground state of $Co(mnt)_2^{2-}$ has been the subject of recent controversy.[1a] At the present time, most of our solid and solution susceptibility measurements on a wide variety of pure analyzed samples seem to support the contention that this compound is an effective spin doublet. However, the magnetic moment of $Co(mnt)_2^{2-}$ is definitely influenced by the nature of the cation in solid samples, with certain complexes possessing substantially higher moments than the 1.95 B.M. expected for $S = {}^1/_2$ and the measured $\langle g \rangle$ of 2.255. Thus, much spectral and magnetic work remains to be done on this system before the exact magnetic ground state can be rigorously and finally established. We plan to present all our results on the $Co(mnt)_2^{2-}$ system after completing investigations now in progress.

We presently have polarographic evidence and chemical evidence for the existence of $Co(tdt)_2^{2-}$ in solution, but pure samples of this compound have not yet been isolated. It is expected that its magnetic properties will resemble those of $Co(mnt)_2^{2-}$.

The $Rh(mnt)_2^{2-}$ complex is of special interest since it is the first example of a planar, mononuclear Rh(II) complex with $S = {}^1/_2$. The analogous $Rh(tdt)_2^{2-}$ complex has not been prepared yet, but it should exist.

Monoanions. The series of tdt and mnt monoanionic complexes presents 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 also have $S = {}^1/_2$. The latter undergo spin–spin exchange in the solids with the resulting quenching of the expected magnetic moment.[10] This

---

(9) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, **3**, 663 (1964).

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

Table VII. Positions (cm.$^{-1}$) of Some Major Spectral Bands of $M(tdt)_2^-$ Complexes in Various Solvents

	CH_2Cl_2	Acetone	DMF	DMSO	Pyridine	CH_3CN
$Cu(tdt)_2^-$	15,600	15,600	15,600	15,600	15,600	15,600
$Ni(tdt)_2^-$	11,230	11,230	11,230	11,230	11,230	11,230
$Co(tdt)_2^-$	15,200	15,200	15,200	15,200	15,200	15,200
$Fe(tdt)_2^-$	17,800	17,800	20,100	20,350	19,400	19,050

Table VIII. Magnetic Susceptibilities (B.M.) of mnt and tdt Complexes in Various Solvents

	Cyclohexanone	DMF	DMSO	Pyridine
$Cu(tdt)_2^-$	*a*	Diamagnetic	Diamagnetic	Diamagnetic
$Ni(tdt)_2^-$	*a*	2.20	*a*	*a*
$Co(tdt)_2^-$	3.37[b]	3.33	3.43	3.39
$Co(mnt)_2^-$	Diamagnetic	*a*	2.81	Diamagnetic
$Fe(tdt)_2^-$	*a*	*a*	3.87	3.77
$Fe(mnt)_2^-$	3.75	3.82	3.87	4.03

[a] Not measured. [b] Value in acetone.

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. Repeated susceptibility measurements on analytically pure solid samples containing $Fe(tdt)_2^-$ and $Fe(mnt)_2^-$ indicate an $S = {}^1/_2$ ground state for these complexes. 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.[10] The mechanism for this process was considered to involve spin–spin interactions of sulfurs 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 spin doublet, and that the higher moments in solution are the result of interaction of the anions with solvent. The electronic spectrum of $Fe(tdt)_2^-$ is extensively perturbed by solvents, as discussed in the next section. 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.

Solvent and Ligand Perturbations. As we mentioned earlier, there is excellent electronic spectral and e.s.r. evidence that for the dianionic planar mnt complexes there is no significant interaction in the fifth and sixth coordination positions with solvent or other additional ligands.[7,9] Furthermore, most of the monoanionic complexes of mnt and tdt show no appreciable ligand interaction, as judged by the constancy of their electronic spectra in a variety of solvents, some with good coordinating ability. Thus the electronic spectra of the $M(tdt)_2^-$ complexes (M = Cu, Ni, Co) are almost unaltered as the solvent is changed from methylene chloride to DMF or DMSO. Likewise, magnetic susceptibility determinations for $Co(tdt)_2^-$ in a variety of solvents, including pyridine, give essentially identical results.

Certain of the monoanionic complexes, however, do show solvent effects. The $Co(mnt)_2^-$ complex possesses a spin-triplet ground state in DMSO, although in the solid and in cyclohexanone solution this complex is diamagnetic. In pyridine solution $Co(mnt)_2^-$ is diamagnetic and exhibits an electronic spectrum quite unlike that observed in cyclohexanone. A stable five-coordinate complex, $[(n\text{-}C_4H_9)_4N][Co(mnt)_2(py)]$, has been isolated from the solution, and stable adducts are formed with a number of other electron-donor molecules.[8] Apparently the bis-tdt planar matrix system is more effective than the bis-mnt system in resisting further coordination.

The $Fe(tdt)_2^-$ and $Fe(mnt)_2^-$ complexes both have magnetic moments corresponding to spin doublets in solids. However, both complexes are spin quartets in all solvents investigated. The positions of the electronic spectral bands for $Fe(tdt)_2^-$ are solvent dependent, and a stable pyridine adduct, $[Fe(tdt)_2(py)]^-$, has been isolated as the $(n\text{-}C_4H_9)_4N^+$ salt. The relevant spectral and magnetic properties of the monoanions are summarized in Tables VII and VIII, respectively.

Very powerfully coordinating ligands such as *o*-phenanthroline and *o*-phenylenebis(dimethylarsine) react with $Co(tdt)_2^-$ to give adducts, and the former also reacts with $Fe(tdt)_2^-$ presumably to give an adduct, although the latter complex has not been characterized. However, even such good donors as triphenylphosphine

Table IX. Comparison of Solution E.s.r. Results of Certain Planar Metal Complexes[a]

Complex	Solution	$\langle g\rangle$	$\langle a\rangle$, gauss	Ref.
$Cu(mnt)_2^{2-}$	DMF	2.0458	75.63 (^{63}Cu, ^{65}Cu)	9
$Cu(tdt)_2^{2-}$	DMF	2.046	77.6 (^{63}Cu, ^{65}Cu)	This work
$Cu(dtc)_2^{2-}$	DMF	2.0445	81.87 (^{63}Cu, ^{65}Cu)	9
$Cu(dto)_2^{2-}$	DMF	2.0440	81.34 (^{63}Cu, ^{65}Cu)	9
$Ag(mnt)_2^{2-}$	Acetonitrile	2.019	31.4 (^{107}Ag, ^{109}Ag)	This work
$Au(mnt)_2^{2-}$	DMF–diglyme	2.009	41.7 (^{197}Au)	This work
$Ni(mnt)_2^-$	Acetone	2.063	*b*	*c*
$Ni(tdt)_2^-$	Acetone	2.082	*b*	This work
$Ni(S_2C_2Ph_2)_2^-$	DMSO	2.057	4.5 ± 1 (^{61}Ni)	*c*
$Pd(mnt)_2^-$	DMF–$CHCl_3$	2.024	7.7 ± 0.3 (^{105}Pd)	*c*
$Pt(mnt)_2^-$	DMF–$CHCl_3$	2.042	82 ± 7 (^{195}Pt)	*c*
$Pt(tdt)_2^-$	Acetone	2.031	*b*	This work
$Co(mnt)_2^{2-}$	Acetone	2.255	*b*	*d*
$Co(S_2C_2Ph_2)_2^{2-}$	Diglyme	2.33	*b*	This work
$Pd(tdt)_2^-$	DMF	2.022	*b*	This work

[a] All measurements were made at room temperature. [b] No hfs resolved. [c] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963). [d] Davison, *et al.*, footnote *b*, Table V.

Table X. Anisotropic *g* Values Measured for Solid Samples Containing $M(mnt)_2^{n-}$ and $M(tdt)_2^{n-}$[a]

Complex	Solid sample	g_1	g_2	g_3
$Cu(mnt)_2^{2-}$	Methanol glass, 77°K.	$g_{xx,yy}$ = 2.0283	g_{zz} = 2.0820	
	Single crystal diluted in $[(n\text{-}C_4H_9)_4N]_2[Ni(mnt)_2]$	2.023 (x)	2.026 (y)	2.086 (z)[b]
$Ni(mnt)_2^-$	Single crystal diluted in $[(n\text{-}C_4H_9)_4N][Cu(mnt)_2]$	1.998 (z)	2.042 (x)	2.160 (y)[b]
$Ni(tdt)_2^-$	DMF–$CHCl_3$ glass, 100°K.	2.016	2.048	2.183
$Pd(mnt)_2^-$	DMF–$CHCl_3$ glass, 100°K.	1.956	2.046	2.065[c]
$Pt(mnt)_2^-$	DMF–$CHCl_3$ glass, 100°K.	1.825	2.067	2.221[c]
$Pt(tdt)_2^-$	DMF–$CHCl_3$ glass, 77°K.	1.810	2.059	2.229
$Co(mnt)_2^{2-}$	Single crystal diluted in $[(n\text{-}C_4H_9)_4N]_2[Ni(mnt)_2]$	1.977 (z)	2.025 (x)	2.798 (y)[a]
$Rh(mnt)_2^{2-}$	Single crystal diluted in $[(n\text{-}C_4H_9)_4N]_2[Ni(mnt)_2]$	1.936 (z)	2.019 (x)	2.447 (y)[a]

[a] Reference coordinate system in Figure 1. [b] See ref. 11. [c] See Footnote *c*, Table IX.

and triphenylarsine fail to react with $Co(tdt)_2^-$, and the spectra of $Cu(tdt)_2^-$ and $Ni(tdt)_2^-$ are essentially unaltered in various media, including a solution containing *o*-phenanthroline. These findings again demonstrate very strikingly the exceptional aptitude of the bis-tdt matrix system for stabilizing metal ions in a square-planar situation.

E.s.r. Results. The solution e.s.r. results for a representative assortment of related sulfur-donor, planar metal complexes with spin-doublet ground states are given in Table IX. It is quite striking that for a particular metal the $\langle g\rangle$ values are nearly independent of the exact nature of the sulfur-donor ligand. For example, we have the following characteristic $\langle g\rangle$ value ranges for the complexes cited.

$[CuS_4]$ ($S = {}^1/_2$) $\langle g\rangle$ between 2.0440 and 2.0458
$[NiS_4]$ ($S = {}^1/_2$) $\langle g\rangle$ between 2.057 and 2.082
$[PdS_4]$ ($S = {}^1/_2$) $\langle g\rangle$ between 2.022 and 2.024
$[PtS_4]$ ($S = {}^1/_2$) $\langle g\rangle$ between 2.031 and 2.042
$[CoS_4]$ ($S = {}^1/_2$) $\langle g\rangle$ between 2.255 and 2.33

It appears that only the cobalt complexes (and the single rhodium complex) have $\langle g\rangle$ values substantially greater than the free-electron value.

The splittings due to electron–(metal nucleus) interactions are also given in Table IX. The $^{63,65}Cu$ splittings are in the range 75–82 gauss, quite comparable to the splittings observed in Cu(II) complexes containing nitrogen- and oxygen-donor ligands.[1a] This indicates that the metal character of the σ^* (xy) molecular orbital is probably about the same in all these complexes. The very small splitting of 4.5 ± 1 gauss due to ^{61}Ni ($I = {}^3/_2$) in $Ni(S_2C_2Ph_2)_2^-$ is taken as evidence of the dominant ligand character of the π symmetry orbital below $\sigma^*(xy)$ in these complexes.

The two lines due to $^{107,109}Ag$ and the four lines due to ^{197}Au are clearly resolved in the e.s.r. spectra of $Ag(mnt)_2^{2-}$ and $Au(mnt)_2^{2-}$, respectively.

The anisotropic *g* values obtained from the e.s.r. spectra of various types of solid samples (single crystal, polycrystalline, frozen glass) containing bis-mnt and bis-tdt complexes are given in Table X. For $Cu(mnt)_2^{2-}$ and $Cu(tdt)_2^{2-}$, $g_1 = g_2 = g_{xx,yy}$ and $g_3 = g_{zz}$, with $g_{zz} > g_{xx,yy}$. The values of $g_{xx,yy}$ and g_{zz} are much smaller in the CuS_4 complexes than in typical CuO_4 and CuO_2N_2 complexes. This is further evidence that, although the unpaired electron is in a metal-based $\sigma^*(xy)$ orbital, the highest-filled levels of $x^2 - y^2$ and xz or yz symmetries are *predominantly ligand based* in the CuS_4 series. Thus the low-energy excited states due to excitations of the types $x^2 - y^2 \rightarrow xy$ and $xz(yz) \rightarrow xy$ do not contribute as significantly to raising the *g* values from 2.0023 as excitations of the same types in the CuO_4 and CuO_2N_2 complexes.

All the electronically similar complexes with an unpaired electron in a π symmetry orbital exhibit similar e.s.r. spectra. There are three distinctly different *g*

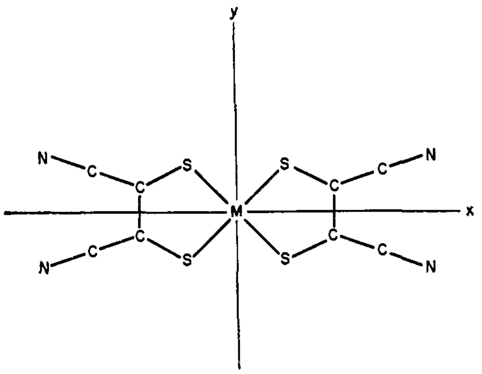


Figure 1. Coordinate system for $M(mnt)_2^{n-}$ for designation of molecular orbitals.

values. For example, $Ni(mnt)_2^-$ has $g_1 = 1.998$, $g_2 = 2.042$, and $g_3 = 2.160$. Single crystal e.s.r. studies have established that, for the coordinate system shown in Figure 1, $g_1 = g_{zz}$, $g_2 = g_{xx}$, and $g_3 = g_{yy}$ in the $Ni(mnt)_2^-$, $Co(mnt)_2^{2-}$, and $Rh(mnt)_2^{2-}$ complexes.[11] There is reason to suspect that this assignment of internal axes will hold for all the complexes given in Table X which have the same ground-state electronic structure.

Electronic Structures and Spectral Properties. A complete MO calculation has been carried out for the $Ni(mnt)_2^{n-}$ system,[7] and we shall use the results of this calculation as a guide in assigning the electronic structures of the bis-mnt and bis-tdt complexes. For the coordinate system shown in Figure 1, the relative energies of the most important molecular orbitals are shown in Figure 2. The orbitals called $\pi(L)$ and $\pi^*(L)$ are essentially pure ligand levels. The $\pi(L) \leftrightarrow \pi^*(L)$ separation is determined by the position of the *first* intraligand ($L \rightarrow L^*$) band in a complex. In the electronic ground states of the metal complexes under discussion here, $\pi(L)$ will always be filled with electrons and $\pi^*(L)$ will always be empty.

There are three other nondegenerate orbitals of great importance, labeled π_2, π_1, and $\sigma^*(xy)$ in order of increasing energy. For $Ni(mnt)_2^{2-}$ and $Ni(mnt)_2^-$, certain theoretical and experimental evidence indicates that π_2 has xz symmetry and π_1 has $x^2 - y^2$ symmetry.[12] Furthermore, several independent experiments indicate that $\sigma^*(xy)$ is mainly metal based, while π_2 and π_1 are mainly ligand based in these complexes.[1a,e] However, to preserve the generality of the model we shall assume only that both mnt and tdt complexes have a relatively unstable $\sigma^*(xy)$ level, with two nondegenerate levels of π symmetry of lower energy. The separation of σ^* and π_1 is called Δ_1 and Δ_2 is the $\pi_1 \leftrightarrow \pi_2$ separation. The low-energy, low-intensity electronic spectra of $Cu(mnt)_2^-$, $Ni(mnt)_2^-$, and $Cu(tdt)_2^-$ establish the energy-level pattern shown in Figure 2. The spectra of all these $(\pi_2)^2(\pi_1)^2$ ground-state complexes are compared in Table XI. There are two low-intensity bands in every case, assigned $\pi_1 \rightarrow \sigma^*$ and $\pi_2 \rightarrow \sigma^*$, respectively. From the band positions given, we see that $\Delta_1[Ni(tdt)_2^{2-}] > \Delta_1[Ni(mnt)_2^{2-}] > \Delta_1[Cu(tdt)_2^-] > \Delta_1[Cu(mnt)_2^-]$. However, the Δ_2 values of $Cu(mnt)_2^-$ and $Cu(tdt)_2^-$ are approximately the same.

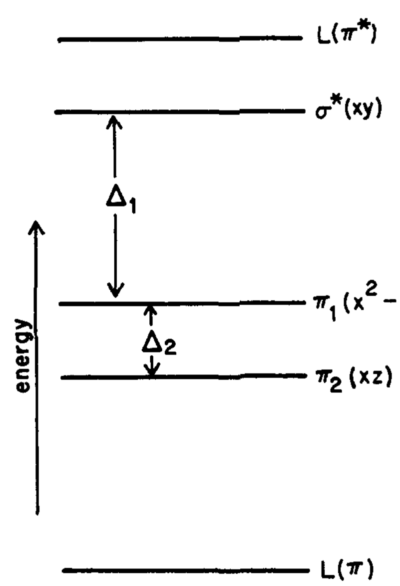


Figure 2. A diagram of the most important energy levels in $Ni(mnt)_2^{n-}$ complexes.

Table XI. Electronic Spectral Assignments for Planar mnt and tdt Complexes with $(\pi_2)^2(\pi_1)^2$ Ground States

	Band positions, cm.$^{-1}$ (ϵ)	
Complex	$\pi_1 \rightarrow \sigma^*(xy)$	$\pi_2 \rightarrow \sigma^*(xy)$
$Cu(mnt)_2^-$	6,400 (337)	13,000 (110)
$Cu(tdt)_2^-$	8,090 (382)	15,600 (318)
$Ni(mnt)_2^{2-}$	11,850 (30)	17,500 (570)
$Ni(tdt)_2^{2-}$	14,540 (35)	19,510 (135)
$Au(mnt)_2^-$	13,400 (44)	21,700 (112)
$Au(tdt)_2^-$	15,550 (87)	23,530 (195)

The molecular orbital configurations of the Co, Ni, and Cu group planar complexes containing mnt and tdt are assigned in Table XII. The low-energy electronic spectra of the $(\pi_2)^2(\pi_1)$ complexes are more complicated than the spectra discussed above for the $(\pi_2)^2(\pi_1)^2$ complexes, owing to the possibility of transitions into the π_1 level. The $\pi_2 \rightarrow \pi_1$ transition is lowest and is parity forbidden, while *certain* transitions

Table XII. Electronic Structures of $M(mnt)_2^{n-}$ and $M(tdt)_2^{n-}$ Complexes

MO configuration				
$S = 0$	$S = 1$	$S = {}^1/_2$	$S = 0$	$S = {}^1/_2$
$(\pi_2)^2$	$(\pi_2)(\pi_1)$	$(\pi_2)^2(\pi_1)$	$(\pi_2)^2(\pi_1)^2$	$(\pi_2)^2(\pi_1)^2(\sigma^*)$
$Co(mnt)_2^-$	$Co(tdt)_2^-$	$Co(mnt)_2^{2-}$ $Rh(mnt)_2^{2-}$ $Ni(mnt)_2^-$ $Ni(tdt)_2^-$ $Pd(mnt)_2^-$ $Pt(mnt)_2^-$ $Pt(tdt)_2^-$	$Ni(mnt)_2^{2-}$ $Ni(tdt)_2^{2-}$ $Pt(mnt)_2^{2-}$ $Pt(mnt)_2^{2-}$ $Pt(tdt)_2^{2-}$ $Cu(mnt)_2^-$ $Cu(tdt)_2^-$ $Au(mnt)_2^-$ $Au(tdt)_2^-$	$Cu(mnt)_2^{2-}$ $Cu(tdt)_2^{2-}$ $Ag(mnt)_2^{2-}$ $Au(mnt)_2^{2-}$

---

(11) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4582 (1964).

(12) However, a calculation of e.s.r. parameters using metal d-orbital functions indicates[11] a probable ground-state structure $(xz)^1$ for $Ni(mnt)_2^-$. We have questioned[16] the reliability of this type of calculation for a complex in which the unpaired electron is predominantly localized on the ligand atoms.

labeled generally as $\pi(L) \rightarrow \pi_1$ are fully allowed. Thus, in favorable cases, it has been possible to resolve a low-energy, low-intensity band assigned $\pi_2 \rightarrow \pi_1$ and an intense band at higher energy assigned $\pi(L) \rightarrow \pi_1$. The positions of the $\pi_2 \rightarrow \pi_1$ band for $Ni(mnt)_2^-$ and $Ni(tdt)_2^-$ and the positions of the $\pi(L) \rightarrow \pi_1$ band characteristic of the $(\pi_2)^2(\pi_1)$ complexes are set out in Table XIII for comparison.

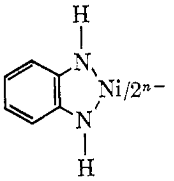
Table XIII. Electronic Spectral Assignments for Planar mnt and tdt Complexes with $(\pi_2)^2(\pi_1)$ Ground States

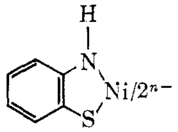
Complex	Band maxima, cm.$^{-1}$ (ϵ) $\pi_2 \rightarrow \pi_1$	$\pi(L) \rightarrow \pi_1$
$Ni(mnt)_2^-$	8330 (329)	11,790 (8,000)
$Ni(tdt)_2^-$	7280 (240)	11,230 (16,270)
$Pd(mnt)_2^-$	*a*	9,000 (13,800)[b]
$Pt(mnt)_2^-$	*a*	11,700 (11,700)[b]
$Pt(tdt)_2^-$	*a*	11,220 (18.000)

[a] Position of this band has not been established. [b] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

We now return to one of the most interesting results in Table XII, that is, the observation of different ground states for $Co(mnt)_2^-$ and $Co(tdt)_2^-$. The difference in the energies of spin-singlet and spin-triplet ground states must be related to the value of Δ_2 in these complexes. This value can be inferred from the positions of the $\pi_2 \rightarrow \pi_1$ band in $Ni(mnt)_2^-$ and $Ni(tdt)_2^-$. The $\pi_2 \rightarrow \pi_1$ band is at 8330 cm.$^{-1}$ in $Ni(mnt)_2^-$ and at 7280 cm.$^{-1}$ in $Ni(tdt)_2^-$. This implies that Δ_2 is approximately 1000 cm.$^{-1}$ *larger* in $Ni(mnt)_2^-$ than in $Ni(tdt)_2^-$, consistent with the spin-triplet ground state for $Co(tdt)_2^-$ and the spin-singlet ground state for $Co(mnt)_2^-$.

Other Planar-Stabilizing Ligands. Recent work has demonstrated[1b,e] that several complexes exist that are quite analogous to the $Ni(tdt)_2^{n-}$ complexes but with nitrogen as the donor atom or one of the donor atoms. For example, two of these systems are shown below





where $n = 0, 1, 2$. The complexes with $n = 1$ have $S = {}^1/_2$ and give characteristic e.s.r. spectra. Thus the unusual $S = {}^1/_2$ nickel system is still obtained on replacement of S with NH in these cases. These observations indicate that it should be possible to stabilize new magnetic states in a planar geometry with appropriate extended π-system ligands containing donor atoms in the nitrogen and oxygen families. With phosphorus, arsenic, and selenium as potentially good donor atoms, it should prove possible to greatly extend the examples of unusual planar complexes and finally provide answers to the interesting questions relating to electronic structure that have been raised thus far with sulfur-donor systems.

Acknowledgments. Acknowledgment is made to the National Science Foundation for support of this research. Partial support was provided by Public Health Service Grant CA-07016-02 from the National Cancer Institute. H. B. G. thanks the Alfred P. Sloan Foundation for a Research Fellowship.