the complex $Ir(CO)Cl_2[P(C_6H_5)_3]_2(p-SO_2C_6H_4CH_3)$ to the corresponding aryl by heating it in boiling toluene. Thus both the SO_2 insertion and the desulfurylation can be effected but so far not on the same system, as is the case with the analogous carbon monoxide reactions.[45] It becomes evident that additional studies are necessary before factors influencing reactions of this general nature are reasonably well understood.

Characterization and Electronic Structures of Metal Complexes Containing Benzene-1,2-dithiolate and Related Ligands

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received May 12, 1966

Abstract: The syntheses and properties of a series of square-planar complexes with the general formula $[(n-C_4H_9)_4N][M(S_2C_6X_2Y_2)_2]$, where M = Co, Ni, and Cu (X = Y = H, CH_3, Cl; X = H, Y = CH_3), are reported. Spectral and magnetic properties, as well as polarographic half-wave potentials, are strongly dependent on the electronic nature of the substituent. This is shown to be consistent with an electronic structural model in which the highest filled molecular orbitals are largely ligand in composition. Possible interpretations of the unusual magnetic properties of the $[(n-C_4H_9)_4N][Co(tcdt)_2]$ complex are discussed.

The ligand toluene-3,4-dithiolate (tdt) forms a series of square-planar complexes with interesting magnetic properties.[3] For example, with Ni as central metal, the complexes $Ni(tdt)_2$, $Ni(tdt)_2^-$, and $Ni(tdt)_2^{2-}$ have been characterized.[3,4] It is of interest that the unusual, paramagnetic $(S = 1/2)$ $Ni(tdt)_2^-$ complex is unquestionably the most air stable of the three entries.

In view of the recent interest in metal complexes containing sulfur-donor ligands,[5] we have undertaken studies aimed at the preparation, characterization, and electronic structural study of the monoanionic planar systems of the general formula I. In system I, the

I
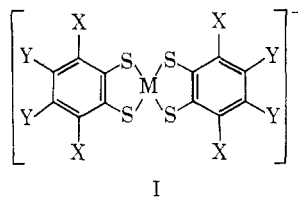
effect of different substituents on the electronic structure of the MS_4 group can be systematically investigated. In this paper, we report our studies on the I complexes with M = Co, Ni, Cu (X = Y = H, CH_3, Cl; X = H, Y = CH_3).

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(3) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 43 (1966).
(4) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965).
(5) (a) S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965); (b) H. B. Gray, *Transition Metal Chem.*, **1**, 239 (1965).

Experimental Section

Preparation of Ligands. Benzene-1,2-dithiol (bdt), o-xylene-4,5-dithiol (xdt), and 3,4,5,6-tetramethylbenzene-1,2-dithiol, or prehnitene-5,6-dithiol (pdt), were prepared according to the method of Adams and Ferretti.[6] Substituted o-dibromobenzenes were treated with cuprous butyl mercaptan to form thioethers which were subsequently cleaved by sodium in liquid ammonia, yielding the substituted benzene-1,2-dithiols.

3,4,5,6-Tetrachlorobenzene-1,2-dithiol (tcdt) was prepared by treating hexachlorobenzene, sodium sulfhydrate, and iron powder in N,N-dimethylformamide at 145°. After reaction was complete, base was added to precipitate the iron complex. The precipitate was collected and boiled with excess zinc oxide in methanol. The mixture was filtered and the filtrate acidified to precipitate the free dithiol. The o-dithiol configuration was verified by a Raney nickel degradation which produced 1,2,3,4-tetrachlorobenzene. Recrystallization from benzene gave a pale yellow compound, mp 265–266°.

Anal. Calcd for $C_6Cl_4S_2H_2$: C, 25.75; Cl, 50.64; S, 22.90; H, 0.72. Found: C, 25.81; Cl, 49.37; S, 24.60; H, 0.75.

Preparation of Complexes. $[(n-C_4H_9)_4N][Co(bdt)_2]$. Benzene-1,2-dithiol (1.6 g, 0.011 mole) was added to potassium metal (0.85 g, 0.022 g-atom) dissolved in 25 ml of absolute ethanol. Addition of a solution of $CoCl_2 \cdot 6H_2O$ (1.19 g, 0.005 mole) in 10 ml of absolute ethanol resulted in an intense dark blue color. A solution of $(n-C_4H_9)_4NBr$ (1.71 g, 0.005 mole) in 15 ml of ethanol was added, and the mixture was cooled in ice and filtered. The precipitate was washed with absolute ethanol and ether and dried. The solid was then dissolved in 200 ml of methylene chloride and filtered, leaving a residue of halide salts. The filtrate was concentrated to 20 ml under reduced pressure and then cooled. A 2.55-g sample of dark blue crystals was collected, washed, and dried as before. This crude material was recrystallized twice from methylene chloride to give 2.05 g of blue-black needles.

The complexes $[n-C_4H_9)_4N][Co(xdt)_2]$ and $[(n-C_4H_9)_4N][Co(pdt)_2]$ were prepared by the same procedure.

(6) (a) R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, **81**, 4927 (1959); (b) *Org. Syn.*, **42**, 22, 54 (1962).

Table I. Analytical Data for [(n-C₄H₉)₄N][M(S₂C₆X₂Y₂)₂] Complexes

Complex	%C Calcd	Found	%H Calcd	Found	%N Calcd	Found	%S Calcd	Found	%Cl Calcd	Found
[(n-C₄H₉)₄N][Co(pdt)₂]	62.30	62.76	8.71	8.64	2.02	2.20	...	...	...	...
[(n-C₄H₉)₄N][Ni(pdt)₂]	62.32	62.17	8.72	8.73	2.02	1.98	18.48	18.70	...	...
[(n-C₄H₉)₄N][Cu(pdt)₂]	61.89	61.79	8.66	8.65	2.00	2.00	...	...	...	...
[(n-C₄H₉)₄N][Co(xdt)₂]	60.25	59.95	8.22	8.09	2.20	2.06	20.10	19.56	...	...
[(n-C₄H₉)₄N][Ni(xdt)₂]	60.27	59.99	8.22	8.24	2.20	2.18	20.11	19.82	...	...
[(n-C₄H₉)₄N][Cu(xdt)₂]	59.82	60.01	8.16	8.41	2.18	1.97	...	...	...	...
[(n-C₄H₉)₄N][Co(bdt)₂]	57.80	58.10	7.62	7.73	2.41	2.60	22.04	20.43	...	...
[(n-C₄H₉)₄N][Ni(bdt)₂]	57.82	58.27	7.62	7.66	2.41	2.55	22.05	21.20	...	...
[(n-C₄H₉)₄N][Cu(bdt)₂]	57.34	57.27	7.56	7.67	2.39	2.63	21.87	22.85	...	...
[(n-C₄H₉)₄N][Co(tcdt)₂]	39.22	39.53	4.23	4.18	1.63	1.70	14.96	15.44	...	...
[(n-C₄H₉)₄N][Ni(tcdt)₂]	39.23	39.15	4.23	4.18	1.63	1.67	...	...	33.09	31.17
[(n-C₄H₉)₄N][Cu(tcdt)₂]	39.01	39.06	4.21	4.17	1.62	1.66	...	...	32.90	31.75
[(n-C₄H₉)₄N][Au(tcdt)₂]	33.78	33.76	3.64	3.57	1.41	1.35	...	...	28.49	29.16
[(n-C₄H₉)₄N][Co(tcdt)₂(PPh₃)]	49.34	49.87	4.62	4.68	1.25	1.20	...	...	...	...
[(n-C₄H₉)₄N][Co(tcdt)₂(o-phen)]	46.30	46.10	4.27	4.35	4.05	3.91	...	...	...	...
[(n-C₄H₉)₄N][Co(pdt)₂(o-phen)]	65.94	62.57	7.84	7.50	4.81	4.31	...	...	...	...

[(n-C₄H₉)₄N][Ni(bdt)₂]. Benzene-1,2-dithiol (1.4 g, 0.01 mole) was added to a solution of potassium metal (0.8 g, 0.02 g-atom) in 25 ml of absolute ethanol. A solution of NiCl₂·6H₂O (1.17 g, 0.005 mole) in ethanol was added, resulting in the formation of a muddy red-brown color. Following this, (n-C₄H₉)₄NBr (1.69 g, 0.005 mole) was added and the mixture allowed to stand with occasional stirring for 3 hr. The color of the mixture gradually turned green, indicating oxidation from a dianionic species to the more stable monoanionic form. The mixture was then filtered, washed, and dried. The green precipitate was treated in the same manner as the [(n-C₄H₉)₄N][Co(bdt)₂] complex, except that absolute ethanol was added to the methylene chloride solution to facilitate crystallization. The final yield was 1.15 g of dark green needles.

The [(n-C₄H₉)₄N][Ni(xdt)₂] and [(n-C₄H₉)₄N][Ni(pdt)₂] complexes were prepared by similar procedures.

[(n-C₄H₉)₄N][Cu(bdt)₂]. To a solution of potassium metal (0.85 g, 0.022 g-atom) in 25 ml of absolute ethanol was added benzene-1,2-dithiol (1.6 g, 0.011 mole), followed by a solution of CuCl₂·2H₂O (0.83 g, 0.005 mole) in ethanol. An intense red-brown color appeared immediately A solution of (n-C₄H₉)₄NBr (1.64 g, 0.005 mole) in absolute ethanol was added. After standing for 3 hr with stirring, the mixture was green throughout. It was cooled and filtered, and the green precipitate was treated in the same manner as the [(n-C₄H₉)₄N][Ni(bdt)₂] complex to give 1.6 g of green crystals.

[(n-C₄H₉)₄N][Cu(xdt)₂] and [(n-C₄H₉)₄N][Cu(pdt)₂] were prepared by the same procedure.

[(n-C₄H₉)₄N][Co(tcdt)₂]. 3,4,5,6-Tetrachlorobenzene-1,2-dithiol (6.0 g, 0.021 mole) was dissolved in 200 ml of tetrahydrofuran (THF). The addition of CoCl₂·6H₂O (2.48 g, 0.011 mole) dissolved in 10 ml of absolute ethanol caused the immediate appearance of a dark blue color. (n-C₄H₉)₄NBr (3.5 g, 0.011 mole) was added. The solution, which had been shaken until the added salt had completely dissolved, was concentrated to 25 ml under reduced pressure. Cooling produced 3.07 g of dark blue-black crystals which were collected by filtration, washed with methanol and ether, and then dried. Recrystallization from methylene chloride produced 2.1 g of fine blue-black crystals.

[(n-C₄H₉)₄N][Ni(tcdt)₂] and [(n-C₄H₉)₄N][Cu(tcdt)₂] were prepared following the procedure used for the [(n-C₄H₉)₄N][Co(tcdt)₂] complex, except that absolute ethanol and methanol were used to promote crystallization.

The tetraphenylarsonium salts of the M(tcdt)₂⁻ complexes were prepared by using Ph₄AsCl in place of (n-C₄H₉)₄NBr at the appropriate place in the procedure.

[(n-C₄H₉)₄N][Au(tcdt)₂]. To a solution of 3,4,5,6-tetrachlorobenzene-1,2-dithiol (3.0 g, 0.011 mole) in 150 ml of THF was added a solution of K[AuCl₄] (2.08 g, 0.0055 mole) in 50 ml of THF. The green-brown mixture was filtered and (n-C₄H₉)₄NBr (2.09 g, 0.006 mole) was added to the filtrate. The mixture was allowed to stand with occasional stirring for 1 hr and was then filtered. The volume of the green solution was concentrated under reduced pressure to 20 ml. Methanol was added slowly to promote crystallization. The light green crystals were collected, washed, and dried. After two recrystallizations from methylene chloride and methanol, beautiful light green crystals were obtained.

[(n-C₄H₉)₄N][Co(tcdt)₂PPh₃]. [(n-C₄H₉)₄N][Co(tcdt)₂] (0.857 g, 0.001 mole) was dissolved in 50 ml of THF. The addition of triphenylphosphine (0.636 g, 0.0024 mole) dissolved in 25 ml of THF caused an immediate color change in the solution from dark blue to an intense red. The solution was concentrated to 15 ml under reduced pressure and absolute ethanol added. Fine red-black crystals were collected, washed with ethanol, and dried.

The red crystals decompose in acetone, giving free triphenylphosphine and Co(tcdt)₂⁻, as indicated by spectral measurements.

[(n-C₄H₉)₄N][Co(tcdt)₂(o-phen)]. A solution of o-phenanthroline (0.306 g, 0.0017 mole) in 25 ml of THF was added to a solution of [(n-C₄H₉)₄N][Co(tcdt)₂] (0.857 g, 0.001 mole) in 50 ml of THF, resulting in the formation of a dark green-brown solution. Concentrating the solution to 15 ml and adding absolute ethanol caused precipitation of a fine olive powder. The adduct was recrystallized from methylene chloride by addition of ethanol; 0.95 g of a fine olive crystalline material was collected. It decomposes readily in acetone, giving Co(tcdt)₂⁻ and free o-phen.

[(n-C₄H₉)₄N][Co(pdt)₂(o-phen)]. To a solution of [(n-C₄H₉)₄N]-[Co(pdt)₂] (0.637 g, 0.001 mole) in 50 ml of THF was added a solution of o-phenanthroline (0.233 g, 0.0013 mole). In contrast to the [(n-C₄H₉)₄N][Co(tcdt)₂(o-phen)] adduct, the solution remained dark blue. Concentrating the solution to a small volume and adding absolute ethanol resulted in the precipitation of a gray-brown powder. It was recrystallized from a methylene chloride solution containing excess o-phenanthroline. As indicated by the analysis, it was difficult to obtain this adduct pure.

Physical Measurements. Electronic spectra were measured using a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used throughout. Solid absorption spectra were taken on mineral oil treated Whatman No. 1 chromatography paper. Magnetic susceptibility measurements were made at room temperature by the Gouy method using Hg[Co(SCN)₄][7] and Cs₂-[CoCl₄] solution[8] as calibrants for solid and solution moments, respectively. Conductances were determined on an Industrial Instruments Model RC16B2 bridge, using a cell calibrated with 0.010 M KCl solution. All solutions were 0.001 M in Spectrograde nitromethane. Polarographic measurements were made in N,N-dimethylformamide solution in a three-electrode cell using an electronic polarograph described elsewhere.[9] Triangular wave chronoamperometry (oscillopolarography) was employed, using a platinum electrode as the indicator electrode. The reference electrode was Ag│AgClO₄ (0.1 M). All solutions were prepared using purified DMF and were 0.1 M in (n-C₃H₇)₄NClO₄ and 0.001 M in complex. A Norelco X-ray machine with copper Kα radiation and a nickel filter was used for measuring X-ray powder patterns.

Results

Analytical data for the [(n-C₄H₉)₄N][M(S₂C₆X₂Y₂)₂] complexes are given in Table I. Colors, conductances,

(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1985).
(8) B. N. Figgis, *ibid.*, 3423 (1964).
(9) M. J. Kelley, J. D. Fisher, and K. C. Jones, *Anal. Chem.*, **31**, 1475 (1959); **32**, 1262 (1960).

Table II. Physical Properties of the $[(n\text{-}C_4H_9)_4N][M(S_2C_6X_2Y_2)_2]$ Complexes

Complex	Color	Mp, °C	Λ, cm^2 ohm^{-1} M^{-1}	μ_{eff} (solid), BM
$[(n\text{-}C_4H_9)_4N][Co(pdt)_2]$	Blue	253	59	3.23
$[(n\text{-}C_4H_9)_4N][Ni(pdt)_2]$	Dark green	242	57	1.82
$[(n\text{-}C_4H_9)_4N][Cu(pdt)_2]$	Green	239	58	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Co(xdt)_2]$	Blue	220	58	3.24
$[(n\text{-}C_4H_9)_4N][Ni(xdt)_2]$	Dark green	215	65	1.83
$[(n\text{-}C_4H_9)_4N][Cu(xdt)_2]$	Green	207	59	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Co(bdt)_2]$	Blue	177	71	3.27
$[(n\text{-}C_4H_9)_4N][Ni(bdt)_2]$	Dark green	173	69	1.83
$[(n\text{-}C_4H_9)_4N][Cu(bdt)_2]$	Green	178	74	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Co(tcdt)_2]$	Blue-black	214	60	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Ni(tcdt)_2]$	Dark green	194	61	1.89
$[(n\text{-}C_4H_9)_4N][Cu(tcdt)_2]$	Green	192	60	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Au(tcdt)_2]$	Light green	179	55	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Co(tcdt)_2(PPh_3)]$	Red	159	..	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Co(tcdt)_2(o\text{-phen})]$	Green-brown	248	..	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Co(pdt)_2(o\text{-phen})]$	Gray	$\sim$165 (α)	..	Diamagnetic

Table III. Magnetic Moments of the $Co(tcdt)_2{}^-$, $Co(pdt)_2{}^-$, and $Co(mnt)_2{}^-$ Complexes

		μ_{eff}, BM
$[(n\text{-}C_4H_9)_4N][Co(tcdt)_2]$	Solid	Diamagnetic
	Cyclohexanone soln	3.14
	Tetrahydrofuran soln	3.18
	Dimethyl sulfoxide soln	2.37
	Pyridine soln	Diamagnetic
$[(n\text{-}C_4H_9)_4N][Co(pdt)_2]$	Solid	3.23
	Pyridine soln	3.33
$[(n\text{-}C_4H_9)_4N][Co(mnt)_2]$	Solid	Diamagnetic
	Cyclohexanone soln	Diamagnetic
	Dimethyl sulfoxide soln	2.81
	Pyridine soln	Diamagnetic

melting points, and solid magnetic moments are given in Table II. The magnetic properties of the $[(n\text{-}C_4H_9)_4]\text{-}[Co(tcdt)_2]$ complex (in solid and solution) are compared with those of $[(n\text{-}C_4H_9)_4N][Co(pdt)_2]$ and $[(n\text{-}C_4H_9)_4N]\text{-}[Co(mnt)_2]$ in Table III. The complexes all appear to be 1:1 electrolytes in nitromethane solution.[10]

X-Ray Diffraction Results. X-Ray powder diffraction spectra for the metal complexes are given in Table IV. The $R[M(pdt)_2]$ and $R[M(xdt)_2]$ with M = Co, Ni, and Cu are isomorphous within each series. Only the Co and Ni complexes of the type $R[M(bdt)_2]$ have similar X-ray diffraction spectra. The $R[M(tcdt)_2]$ complexes are isomorphous for M = Ni, Cu, Au and R = $[(n\text{-}C_4H_9)_4N]$ and for M = Ni, Cu when R = $[Ph_4As]$. The various complex anions are assumed to be planar in analogy to the related $[M(mnt)_2]^{n-}$ system.[11-14]

Although not isomorphous with the other R[M-(bdt)_2] complexes, the $[(n\text{-}C_4H_9)_4N][Cu(bdt)_2]$ complex most likely contains square-planar complex anions. The difference in the various diffraction spectra probably results from different packing of anion and cation units in the crystal.

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

(11) C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 107 (1966).

(12) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(13) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1500 (1964).

(14) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, **3**, 1507 (1964).

Different packing of anion and cation monomer units in the crystal could also cause the different X-ray diffraction spectra observed for the $R[M(tcdt)_2]$ complexes. Another very reasonable possibility is that the $R[Co(tcdt)_2]$ complex consists of $[Co(tcdt)_2]_2{}^{2-}$ dimer units in the solid. It should be noted that the $[Co(C_4S_4(CF_3)_4]$ complex has recently been shown to have a dimer structure in the solid.[15] Effective dimerization of anion units also occurs in the $R[Ni(mnt)_2]$ crystal, as shown by the observed Ni$\cdots$S distance of 3.59 Å within dimer units as compared to a Ni$\cdots$S distance of 3.75 Å between different dimers.[11] A single crystal X-ray structure of $[(n\text{-}C_4H_9)_4N][Co(tcdt)_2]$ is presently being undertaken to answer this question.[15a]

Polarographic Results. The polarographic half-wave potentials for the substituted benzenedithiol complexes are given in Table V. The relevant data for the bis-(tdt) and bis(mnt) complexes have been included for comparison.

For complexes of the same metal and charge type, the tremendous variation of half-wave potentials observed on changing substituents is immediately evident. The difference in half-wave potentials between pdt and the tcdt complexes of the same metal is approximately 0.7 v for all three metals. This large difference may be correlated with the electronic nature of the substituent. Electron-releasing substituents such as methyl form more stable monoanions or neutral complexes whereas electron-withdrawing chloro substituents favor the dianionic form. The trend within the methyl-substituted series clearly shows the effects of adding relatively electron-releasing groups. The addition of one methyl group stabilizes the monoanion, relative to the dianion, by approximately 0.05 v.

These results show that the ligand must be participating to a large extent in the electron-transfer process. This conclusion lends more support to an electronic structural model in which the ligand has radical-anion character to an extent that varies with its electron-rich or electron-poor nature. It is apparent that classical

(15) J. H. Enemark and W. N. Lipscomb, *ibid.*, **4**, 1729 (1965).

(15a) Note Added in Proof. The X-ray studies are now complete and show a dimeric $[Co(tcdt)_2]_2{}^{2-}$ structure in the crystal. The basic coordination structure is the same as reported for $[CoS_4C_4(CF_3)_4]_2$ in ref 15. In view of its magnetic properties, however, $Co(tcdt)_2{}^-$ appears to be monomeric in THF and cyclohexanone solutions.

Table IV. X-Ray Diffraction Results for the $R[M(S_2C_6X_2Y_2)_2]$ Complexes

Complex	Interplanar spacings (A) of most prominent peaks
$[(n\text{-}C_4H_9)_4N][Co(pdt)_2]$	12.62 (vs), 11.78 (m), 8.70 (m), 8.01 (m), 7.62 (w), 7.26 (s), 6.14 (w), 5.62 (m), 5.24 (m), 5.16 (w), 4.43 (w), 4.15 (vs), 3.93 (s), 3.50 (s), 3.23 (w)
$[(n\text{-}C_4H_9)_4N][Ni(pdt)_2]$	12.65 (vs), 11.78 (s), 8.66 (m), 7.96 (m), 7.61 (m), 7.28 (s), 6.11 (m), 5.60 (m), 5.27 (m), 5.07 (m), 4.39 (w), 4.13 (vs), 3.91 (s), 3.49 (s), 3.22 (w)
$[(n\text{-}C_4H_9)_4N][Cu(pdt)_2]$	12.62 (vs), 11.72 (s), 8.72 (s), 7.96 (m), 7.61 (m), 7.24 (s), 6.14 (m), 5.63 (m), 5.25 (m), 5.08 (m), 4.40 (m), 4.13 (vs), 3.93 (s), 3.49 (s), 3.23 (w)
$[(n\text{-}C_4H_9)_4N][Co(xdt)_2]$	11.30 (vs), 8.37 (s), 7.76 (m), 7.05 (w), 6.62 (m), 6.15 (w), 4.89 (m), 4.70 (m), 4.30 (w), 4.13 (s), 3.87 (vs), 3.53 (w), 3.13 (m)
$[(n\text{-}C_4H_9)_4N][Ni(xdt)_2]$	11.35 (vs), 8.35 (m), 8.02 (m), 7.69 (vs), 7.08 (w), 6.55 (s), 4.90 (w), 4.68 (s), 4.28 (s), 3.94 (vs), 3.56 (m), 3.14 (m)
$[(n\text{-}C_4H_9)_4N][Cu(xdt)_2]$	11.38 (vs), 8.42 (s), 7.77 (s), 7.08 (w), 6.65 (m), 6.26 (m), 4.91 (m), 4.77 (s), 4.22 (s), 3.91 (vs), 3.55 (m), 3.13 (w)
$[(n\text{-}C_4H_9)_4N][Co(bdt)_2]$	9.38 (s), 8.30 (w), 7.74 (vs), 6.80 (m), 6.24 (m), 5.27 (m), 4.82 (s), 4.29 (m), 4.05 (vs), 3.80 (m), 3.54 (w)
$[(n\text{-}C_4H_9)_4N][Ni(bdt)_2]$	9.44 (s), 8.35 (w), 7.77 (vs), 6.86 (m), 6.24 (m), 5.27 (m), 4.84 (s), 4.29 (m), 4.07 (vs), 3.81 (m), 3.54 (w)
$[(n\text{-}C_4H_9)_4N][Cu(bdt)_2]$	9.62 (m), 8.98 (m), 8.15 (s), 6.70 (w), 6.37 (w), 5.43 (w), 4.36 (w), 4.27 (w), 4.07 (vs), 3.22 (w)
$[(n\text{-}C_4H_9)_4N][Co(tcdt)_2]$	11.35 (vs), 10.43 (s), 9.49 (w), 7.70 (s), 5.77 (m), 4.55 (m), 3.77 (m), 3.57 (s), 3.29 (m)
$[(n\text{-}C_4H_9)_4N][Ni(tcdt)_2]$	12.43 (m), 11.73 (s), 8.75 (m), 7.87 (s), 7.20 (s), 6.17 (m), 5.60 (s), 5.02 (m), 4.37 (m), 4.14 (vs), 4.05 (m), 3.91 (vs), 3.50 (s), 3.21 (m)
$[(n\text{-}C_4H_9)_4N][Cu(tcdt)_2]$	12.24 (s), 11.45 (m), 9.76 (m), 7.85 (s), 7.21 (m), 5.76 (m), 5.03 (m), 4.23 (m), 4.16 (s), 3.96 (vs), 3.91 (m), 3.51 (m)
$[(n\text{-}C_4H_9)_4N][Au(tcdt)_2]$	12.43 (s), 11.52 (m), 8.20 (m), 7.81 (m), 7.16 (m), 6.17 (m), 5.57 (w), 4.35 (w), 4.27 (s), 4.15 (s), 3.90 (m), 3.50 (m), 3.20 (m)
$[Ph_4As][Co(tcdt)_2]$	13.93 (s), 12.48 (s), 11.15 (w), 8.51 (m), 8.24 (m), 7.73 (s), 6.55 (m), 5.56 (m), 4.73 (m), 4.46 (s), 4.10 (m), 3.97 (s), 3.70 (m), 3.35 (m), 3.26 (m)
$[Ph_4As][Ni(tcdt)_2]$	10.96 (m), 10.09 (m), 9.46 (m), 8.25 (w), 7.13 (s), 6.35 (m), 5.43 (w), 5.02 (w), 4.79 (m), 4.43 (s), 4.16 (s), 4.02 (s), 3.85 (m), 3.41 (m), 3.26 (w)
$[Ph_4As][Cu(tcdt)_2]$	10.88 (m), 10.06 (w), 9.46 (m), 7.14 (s), 6.37 (m), 5.42 (m), 5.02 (m), 4.80 (m), 4.40 (s), 4.17 (s), 4.03 (s), 3.86 (m), 3.42 (m), 3.28 (m)

Table V. Polarographic Half-Wave Potentials for the One-Electron Reduction of the $ML_2{}^-$ Complexes[a]

$$ML_2{}^- + e^- \rightleftharpoons ML_2{}^{-2}$$

Ligand	$E_{1/2}$, V			
	Co	Ni	Cu	Au
pdt	−1.57	−1.24	−1.41	
xdt	−1.46	−1.14	−1.21	
tdt	−1.41	−1.07	−1.15	
bdt	−1.38	−1.05	−1.14	
tcdt	−0.847	−0.532	−0.752	−1.67
mnt	−0.384	−0.218	−0.201	

[a] Measured in DMF solution relative to Ag|AgClO$_4$ reference electrode.

oxidation formalism cannot adequately describe these complexes.[4]

Magnetic and Spectral Properties. The magnetic moments of the metal complexes are presented in Tables II and III. Positions of major electronic spectral bands under various conditions are given in Tables VI–VIII.

All the $Cu(S_2C_6X_2Y_2)_2{}^-$ complexes are diamagnetic and show no appreciable electronic perturbations in solution, as judged by the constancy of their electronic spectra in a wide range of solvents. This behavior parallels that already established for the $Cu(mnt)_2{}^-$ and $Cu(tdt)_2{}^-$ complexes.[3]

The $Ni(S_2C_6X_2Y_2)_2{}^-$ complexes are paramagnetic and in solid samples exhibit full moments for one unpaired electron. Thus there is no evidence in this series for spin–spin interaction of the type exhibited by $Ni(mnt)_2{}^-$ in solid samples.[16] In solution, the complexes in which

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

the various X and Y substituents are either CH_3 or H ($Ni(bdt)_2{}^-$, $Ni(tdt)_2{}^-$, $Ni(xdt)_2{}^-$, $Ni(pdt)_2{}^-$) exhibit no electronic spectral variations over a range of solvents from methylene chloride to pyridine. The $Ni(tcdt)_2{}^-$ (X = Y = Cl) complex, however, does interact to some extent with solvent molecules, as indicated by clearly measurable differences in peak positions of its major spectral bands. Presumably the relatively electron-withdrawing chloro groups remove electron density from the vicinity of the central metal atom, and weak but specific axial interaction with solvent molecules becomes more favorable.

In the $Co(S_2C_6X_2Y_2)_2{}^-$ series, the electronic nature of the X and Y substituents is important in determining both the magnetic properties of the solids and the behavior of the complexes in solution. Complexes containing CH_3 and H substituents ($Co(bdt)_2{}^-$, $Co(tdt)_2{}^-$, $Co(xdt)_2{}^-$, $Co(pdt)_2{}^-$) are paramagnetic in solid samples, with moments in the 3.18–3.37 BM range, indicating full spin-triplet ground states. The spectral bands exhibited by these complexes are not perturbed significantly in going from methylene chloride to pyridine as solvent. In addition, the spin-triplet magnetic moment for $Co(pdt)_2{}^-$ is not appreciably changed in going from a solid sample to a pyridine solution.

The $R[Co(tcdt)_2]$ complex is diamagnetic in the solid. In both cyclohexanone and tetrahyrofuran solutions, $Co(tcdt)_2{}^-$ is paramagnetic, with moments of 3.14 and 3.18 BM, respectively. In the more strongly coordinating solvent dimethyl sulfoxide (DMSO), the spectral bands of $Co(tcdt)_2{}^-$ are substantially shifted from their positions in tetrahydrofuran and cyclohexanone, and the solution magnetic moment has the lower value of 2.37 BM. In the strong coordinating solvent pyridine, the

Table VI. Positions of Some Major Spectral Bands in $Cu(S_2C_6X_2Y_2)_2{}^-$ Complexes[a]

$Cu(pdt)_2{}^-$	$Cu(xdt)_2{}^-$	$Cu(bdt)_2{}^-$	$Cu(tcdt)_2{}^-$
8,425 (260)	7,800 (420)	8,300 (300)	8,875 (200)
15,550 (350)	15,000 (320)	15,900 (310)	17,200 (300)
24,500 (30,000)	25,100 (27,000)	25,400 (30,000)	24,600 (44,000)

[a] Units of cm^{-1} for methylene chloride solutions of $[(n-C_4H_9)_4N][Cu(S_2C_6X_2Y_2)_2]$. Molar extinction coefficients are in parentheses. The measured electronic spectra of these complexes in pyridine and acetonitrile are virtually the same as those reported in methylene chloride.

Table VII. Positions of Some Major Spectral Bands in $Ni(S_2C_6X_2Y_2)_2{}^-$ Complexes[a]

$Ni(pdt)_2{}^-$	$Ni(xdt)_2{}^-$	$Ni(bdt)_2{}^-$	$Ni(tcdt)_2{}^-$
7,550 (350)	7,450 (310)	7,220 (200)	7,150 (250)[b]
10,800 (16,400)	10,900 (15,500)	11,350 (13,200)	11,300 (15,700)
19,400 (250)	19,500 (330)	19,800 (340)	19,600 (280)

[a] Band maxima are reported in cm^{-1} units for methylene chloride solutions of $[(n-C_4H_9)_4N][Ni(S_2C_6X_2Y_2)_2]$. Molar extinction coefficients are in parentheses. Band positions are essentially the same in acetonitrile and pyridine solutions unless otherwise noted. [b] Absorption in this region for $Ni(tcdt)_2{}^-$ is solvent dependent as follows: acetonitrile, 6900 (220); 8400 (90); pyridine, 6670 (175), 7950 (72); solid absorption in mineral oil, 7550.

Table VIII. Positions of Some Major Spectral Bands in $Co(S_2C_6X_2Y_2)_2{}^-$ Complexes

Complex	Solution	Absorption maxima, cm^{-1} (ϵ)
$[(n-C_4H_9)_4N][Co(pdt)_2]$	CH_2Cl_2[a]	5820 (40); 9300 (75); 14,700 (10,300)
$[(n-C_4H_9)_4N][Co(xdt)_2]$	CH_2Cl_2[a]	5780 (30); 9440 (75); 14,900 (13,000)
$[(n-C_4H_9)_4N][Co(bdt)_2]$	CH_2Cl_2[a]	5710 (25); 9540 (45); 15,200 (12,100)
$[(n-C_4H_9)_4N][Co(tcdt)_2]$	CH_2Cl_2	5375 (50); 9530 (100); 15,000 (12,300)
	CH_3CN	5320 (50); 9620 (128); 15,100 (12,400)
	DMSO	6750 (140); 7270 (148); 9350 (185); 15,050 (11,700)
	Pyridine	7950 (14); 16,250 (1300)
	Solid absorption	
	In mineral oil	5270; 6670; 11,100; 14,500

[a] Band positions are essentially the same in acetonitrile and pyridine solutions.

$Co(tcdt)_2{}^-$ solution is diamagnetic and the electronic spectrum indicates severe interaction of the complex with pyridine molecules. This behavior is reminiscent of the properties of $Co(mnt)_2{}^-$, which is diamagnetic in solid $R[Co(mnt)_2]$, has a magnetic moment of 2.81 BM in DMSO solution, and is diamagnetic in pyridine solution.[3] In the pyridine solution, there is evidence for stable five- and six-coordinate species containing one and two molecules of pyridine, respectively.[17] An important difference in $Co(tcdt)_2{}^-$ and $Co(mnt)_2{}^-$ is their behavior in cyclohexanone solution. The $Co(tcdt)_2{}^-$ complex is a full spin triplet in cyclohexanone, whereas $Co(mnt)_2{}^-$ is diamagnetic.

One possible explanation of the interesting magnetic behavior of $Co(tcdt)_2{}^-$ is that the solid contains monomeric complexes with true $S = 0$ ground states. A weak solvent interaction causes the ground state for the basically four-coordinate complex to change to a spin triplet, whereas a strong solvent interaction leads to stable five- and six-coordinate adducts which are diamagnetic. In this framework, the $Co(tcdt)_2{}^-$ complex is assumed to be effectively perturbed by cyclo-

(17) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 2958 (1964).

hexanone, although $Co(mnt)_2{}^-$ is not. There is some spectral evidence that the crossover from spin singlet to spin triplet may be larger in $Co(mnt)_2{}^-$ than in $Co(tcdt)_2{}^-$, as will be discussed later.

Another plausible interpretation of the magnetic properties of $Co(tcdt)_2{}^-$ is that rather strong, probably pairwise, spin–spin interaction of spin-triplet units occurs in solid $R[Co(tcdt)_2]$ with resultant diamagnetism. If this be true, it is curious that the $Ni(tcdt)_2{}^-$ complex shows no observable spin–spin interaction in $[(n-C_4H_9)_4N][Ni(tcdt)_2]$. On the other hand, the $[(n-C_4H_9)_4N][Co(tcdt)_2]$ and $[(n-C_4H_9)_4N][Ni(tcdt)_2]$ complexes have clearly different X-ray powder patterns, indicating different crystal structures.

The very high order of stability shown by the electronically unusual $M(S_2C_6X_2Y_2)_2{}^-$ complexes is noteworthy. In solutions with air present, the ordinary Co(II), Ni(II), and Cu(II) complexes of the type $M(S_2C_6X_2Y_2)_2{}^{2-}$ readily react to give the considerably more stable $M(S_2C_6X_2Y_2)_2{}^-$ species. For the complexes reported here, only the tcdt ones (chloro substituents) experience significant solvent effects on their spectral and magnetic properties. There is also a distinct trend of increasing solvent interaction in going from $M = Cu$ to $M = Co$ in the $M(tcdt)_2{}^-$ complexes. That is, solvent interaction is not evident in $Cu(tcdt)_2{}^-$, it is small but noticeable in $Ni(tcdt)_2{}^-$, and it is significantly evident in both the spectral and magnetic properties of the $Co(tcdt)_2{}^-$ complex. This is interpreted in terms of relative electron density associated with the central metal atom; the central metal should be most electron deficient in the $Co(tcdt)_2{}^-$ complex.

The $Co(tcdt)_2{}^-$ complex forms a stable five-coordinate adduct with triphenylphosphine, and we have isolated $[(n-C_4H_9)_4N][Co(tcdt)_2(PPh_3)]$ as a dark red crystalline solid. Stable pyridine and triphenylphosphine adducts of $Co(mnt)_2{}^-$ have previously been isolated.[17] In addition, a stable six-coordinate complex of $Co(tcdt)_2{}^-$ and o-phenanthroline has been isolated as the olive-green crystalline $[(n-C_4H_9)_4N][Co(tcdt)_2(o-phen)]$ solid. Although there is no evidence for significant solvent interaction in the $Co(S_2C_6X_2Y_2)_2{}^-$ series with CH_3 and H substituents, a six-coordinate adduct complex $[(n-C_4H_9)_4N][Co(pdt)_2(o-phen)]$ has been isolated from solutions containing o-phenanthroline in large excess. This adduct is difficult to obtain in pure form and

readily dissociates to free Co(pdt)$_2^-$ and o-phenanthroline in all solvents we have investigated.

Electronic Structures and Spectral Assignments. The quantitative calculation of molecular orbitals for the Ni(mnt)$_2^{n-}$ system[18] has been the basis for our previous electronic spectral assignments of the M(tdt)$_2^{n-}$ complexes. The substituent effects on the energies of the electronic transitions in the M(S$_2$C$_6$X$_2$Y$_2$)$_2^-$ complexes should provide an important test of these assignments and thus serve to evaluate our electronic structural model.

The relative ordering of the most important energy levels as obtained from the energy-level calculation of Ni(mnt)$_2^{n-}$ is shown in Figure 1. The orbitals designated π(L) and π*(L) are essentially pure ligand levels. The π(L) $\leftrightarrow$ π*(L) separation is determined by the position of the first intraligand L → L* transition in a particular complex. The three nondegenerate orbitals, labeled π_2, π_1, and σ*(xy) in order of increasing energy, are of greatest importance for the assignments of ground-state and low excited-state configurations. The separation of σ* and π_1 is called Δ_1 and Δ_2 is the π_1 → π_2 separation. For Ni(mnt)$_2^{2-}$ and Ni(mnt)$_2^-$, some theoretical and experimental evidence indicates that π_2 has xz symmetry and π_1 has $x^2 - y^2$ symmetry. On the other side, an analysis of esr data for Ni(mnt)$_2^-$ is more nearly consistent with a level scheme in which π_1 has xz symmetry.[19] Thus both schemes are possible and it would seem wise at this stage to use only the labels π_1 and π_2 to designate these levels. In any event, several independent experiments establish that π_2 and π_1 are mainly ligand-based, whereas σ*(xy) probably has enough metal character to be viewed as a substantially metal-based orbital in these complexes.

The Cu(S$_2$C$_6$X$_2$Y$_2$)$_2^-$ complexes have a $(\pi_2)^2(\pi_1)^2$ ground state. The first two low-intensity bands in these complexes are assigned to the parity-forbidden transitions π_1 → σ* and π_2 → σ*, respectively. As can be seen from a comparison of spectra in Table VI, the Δ_1 value is about 500 cm^{-1} larger for the Cu(tcdt)$_2^-$ than for the Cu(pdt)$_2^-$ complex. Relative values of Δ_2 in the Cu(S$_2$C$_6$X$_2$Y$_2$)$_2^-$ complexes may be obtained by taking the difference of the energies of the π_1 → σ* and π_2 → σ* bands and assuming that interelectronic-repulsion effects are similar for each system. This analysis leads to a Δ_2 value for Cu(tcdt)$_2^-$ which is approximately 1200 cm^{-1} larger than for Cu(pdt)$_2^-$. The observed increase in Δ_2 in going from methyl substituents to the relatively electron-withdrawing chloro substituents is better understood in terms of a model in which the π_2 level is of xz symmetry and thus conjugated with the orbital system of the substituted benzene group. We would expect the π(xz) level to be stabilized *relative* to π(x^2 − y^2) as the ring substituents become more electron-withdrawing. The larger Δ_2 for Cu(tcdt)$_2^-$ is also consistent with the possibility that the ground state of Co(tcdt)$_2^-$ is a spin singlet.

The Ni(S$_2$C$_6$X$_2$Y$_2$)$_2^-$ complexes are assigned a $(\pi_2)^2$-

(18) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).
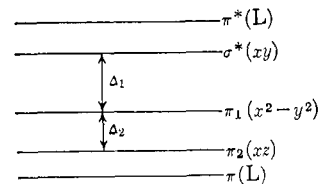(19) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *ibid., Soc.*, **86**, 4582 (1964).

Figure 1. Relative ordering of the most important energy levels from the Ni(mnt)$_2^{n-}$ calculation. The molecule is situated in the xy plane and the x axis bisects the C=C lines.

$(\pi_1)^1$ ground-state configuration. The first low-intensity band in these complexes is logically assigned π_2 → π_1. Reliable relative values of Δ_2 cannot be deduced from the π_2 → π_1 bands for two reasons. First, the π_2 → π_1 band is displayed as a shoulder or minute peak on a very intense broad band and is, therefore, difficult to position with any accuracy. Second, this band in the Ni(tcdt)$_2^-$ complex is subject to solvent perturbations. The value of the π_2 → π_1 transition energy in the Ni(tcdt)$_2^-$ complex ranges from 6670 cm^{-1} in pyridine to 7550 cm^{-1} for a solid sample in mineral oil. The effect of solvent on the spectra of the other Ni complexes is very small. This offers an explanation of the fact that Co(tcdt)$_2^-$ is full spin triplet in cyclohexanone solution, whereas Co(mnt)$_2^-$ remains diamagnetic in that medium. The π_2 → π_1 band for Ni(mnt)$_2^-$ occurs at 8330 cm^{-1} and is not appreciably perturbed by solvents. This indicates a Δ_2 for Ni(mnt)$_2^-$ that is approximately 1000 cm^{-1} greater than that for Ni(tcdt)$_2^-$. If this difference in Δ_2 occurs in the analogous Co complexes, it is possible to understand why a minor solvent perturbation leads to a spin-triplet state for Co(tcdt)$_2^-$, but leaves Co(mnt)$_2^-$ in a diamagnetic state.

The intense, broad band found at about 11 000 cm^{-1} in the Ni(S$_2$C$_6$X$_2$Y$_2$)$_2^-$ complexes is assigned to the L(π) → π_1 transition. The second low-intensity band is in the 20,000-cm^{-1} region and is assigned to the transition π_2 → σ*. The energy difference between the two low-intensity bands allows an estimate for Δ_1 of approximately 12,000 cm^{-1}. This larger Δ_1 value for the Ni series as compared to the Cu series is reasonable. The Δ_1 values for the isoelectronic Ni(tdt)$_2^{2-}$ and Cu(tdt)$_2^-$ complexes are 14,540 and 8090 cm^{-1}, respectively.[3] This analysis predicts that the low-energy transition π_1 → σ* should occur at approximately the same position as the intense 11,000-cm^{-1} band and thus should be effectively buried.

The R[Co(S$_2$C$_6$X$_2$Y$_2$)$_2$] complexes may have either a $(\pi_2)^1(\pi_1)^1$ or a $(\pi_2)^2$ ground state in the solid. In solution all the complexes adopt the spin-triplet ground state. The spectra of the Co(S$_2$C$_6$X$_2$Y$_2$)$_2^-$ complexes are quite complicated and detailed assignments will be reserved until a more quantitative calculation of levels in the M(S$_2$C$_6$X$_2$Y$_2$)$_2^-$ system is available.